THE ELECTROCHEMISTRY OF GASES AND OTHER DIELECTRICS

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FOREWORD

For a number of years, one of the activities of the Conference on Electrical Insulation of the National Research Council has been the publication of monographs on various aspects of the dielectric theory and behavior. The question of electric conduction in gases, in spite of its importance as a cause of failure of many insulating materials and combinations, has proved to be a particularly difficult one to treat in a monograph. Were a rational general theory of ionization by collision, comprising recombination, diffusion of ions, and their motion in the electric field, available, the task of writing a monograph on conduction in gases would be fairly easy. In the absence of a general theory, every expert known to the Committee seemed to be familiar with only a fairly limited phase of the subject, as behavior of a particular gas, ionization within this or that particular range of pressures, or one of the aspects of the theory.

The Committee on Monographs of the Conference on Electrical Insulation was therefore extremely grateful to Professors Glockler and Lind when they consented to collect and digest the widely scattered and voluminous material on the physical and chemical behavior of gases in the electric field, adding the generally accepted elements of the theory. As the work progressed, it became increasingly evident that the volume of available material would greatly exceed the limits of the monograph size agreed upon between the publishers and the committee. The submitted manuscript proved to be, in its thorough and masterly treatment, of more than twice the size limit of a monograph. It was then decided that the work should be published as an independent volume, outside the monograph series, with a hearty endorsement on the part of those of the Conference who had had an opportunity of reading this important manuscript. Thus the present work is, in a sense, an " honorary monograph " of our series.

The book should prove invaluable to those who need the factual material on the chemical behavior of gases in an electric field; this includes the workers on the theoretical aspects of conduction and ionization, for whom it will serve as a convenient compendium of references and data on the subject. Part III should be of particular interest to students of physics and chemistry, in that the physical and theoretical aspects of the behavior of atoms and molecules in discharge regions is treated there in a simple, elementary manner, on the basis of their electronic structure and thermodynamic values, correlated with spectroscopic evidence. The nature of the ions produced, their mobility, and the mechanism of chemical reactions in the electric field are also included.

Thus the authors not only have assembled a vast amount of experimental material, but also have given it such partial interpretation as is possible in the light of our present knowledge of the structure of matter and the nature of the forces involved. The present writer feels confident in extending to the authors the thanks and the congratulations on the part of the Conference on Electrical Insulation and of a large number of physicists and chemists.

VLADIMIR KARAPETOFF

Cornell University
November, 1938

PREFACE

The present work was undertaken at the request of the Committee of Electrical Insulation, Division of Engineering and Industrial Research of the National Research Council, with the object of bringing together the material that might be expected to throw some light on the deterioration in use of liquid dielectrics. It seemed best, however, to treat the entire field of dielectrics, since there is no sharp dividing line between the behavior of liquids and gases under electrical discharge. The particular field of research covered has not yet been summarized and presented in monograph form. It is our hope that the present volume will fill a gap in the literature of the general topic of activation of chemical reactions by various agents. We have attempted to cover the subject of electrical activation by considering all forms of electrical discharge and all types of reactions.

The arrangement of the material was made on the following basis. In Part I, "Typical reactions in various forms of electrical discharge," we have discussed the physical aspects of the various kinds of discharge and have illustrated the reactions taking place by certain researches as examples. The selection was quite arbitrary. Naturally we would make our choice from the latest literature. In our consideration of hydrocarbons in electric discharge we have used our own work, carried out with the support of the American Petroleum Institute, to a large extent because of our familiarity with it.

In Part II, "The chemical reactions in electrical discharges," we have attempted to give a brief account of most of the reactions that have been studied in the various forms of electrical discharge. However, certain special topics such as the production of ozone, its properties and uses and the fixation of nitrogen by electrical processes, have already received attention in special treatises. We have therefore not dealt with these studies in any detail. Doubtless some unintentional omissions will be found, but we have endeavored to make the list of reactions as complete as possible. For convenience the presentation in Part II is arranged in the order of ascending atomic numbers of the elements involved in any given system. For example, one would look for the synthesis or decomposition of water under section 1.8; of hydrogen cyanide under 1.6.7, etc.

In Part III, "The physical and theoretical aspects of discharge reactions," we have included certain topics of physics which we believe must be considered if the chemistry of discharge reactions is to be understood. The theory of the phenomena which contribute to chemical action in electrical discharge is so complicated that it appears hopeless at the present time to present a complete theory of such chemical reactions. Nevertheless, a number of chapters are devoted to the underlying principles. In the last chapter, on the mechanism of ionic chemical reactions, we give the modern theories of such transformations. Throughout the text we have used the ion cluster theory whenever we wished to illustrate and discuss a given reaction. The reasons were mainly simplicity and personal acquaintance with that theory.

The editors of the following journals permitted the reproduction of figures and tables, and we wish to express our thanks to them: Annalen der Physik, Journal of the American Chemical Society, Transactions of the American Electrochemical Society, Engineering, Journal of the Franklin Institute, Journal of the Optical Society of America, Journal of Physical Chemistry, Naturwissenschaften, Physical Review, Proceedings of the Royal Society, Zeitschrift für Elektrochemie, Zeitschrift für Physik, Zeitschrift für physikalische Chemie, Zeitschrift für technische Physik, Bulletin of the University of Illinois Experiment Station.

Of special assistance in the library work, the proof-reading, literature notation, and indexing were Dr. C. H. Schiflett and Mrs. Ruby C. Glockler. We wish to express to them our sincere gratitude. Professor R. S. Livingston has discussed the last chapter with us, and we are grateful for his criticism. Professor V. Karapetoff of Cornell University has been especially helpful in making available to us a series of research reports of the Detroit Edison Co. We wish to thank Dr. C. F. Hirshfeld, Chief of Research, Detroit Edison Co., for the use of this information.

GEO. GLOCKLER
S. C. LIND

October, 1938

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PART I

TYPICAL REACTIONS IN VARIOUS FORMS OF DISCHARGE

ELECTROCHEMISTRY OF GASES AND OTHER DIELECTRICS

CHAPTER I

CHEMICAL REACTION IN THE GLOW DISCHARGE

Introduction. Any region of space filled with matter shows intrinsic electrical conductivity for the reason that cosmic rays produce ionization in the molecules of the material medium. This conductivity can be discovered by means of a device delicate enough to permit the measurement of the current flowing between two conducting surfaces as a function of the applied voltage or by means of an electroscope when one can observe its discharge. Air shows an inherent ionization in this sense. Should we wish to study the chemical effects brought about by this natural ionization due to cosmic rays, we should require more refined methods for ascertaining the occurrence of chemical reactions than we possess at the moment. But besides the natural and all-pervading ionization of material systems due to cosmic rays, there are temporary separations of electrical charges such as lightning flashes which produce intense ionization. Very probably the first observed type of chemical reaction due to electrical phenomena was the formation of ozone and oxides of nitrogen during a lightning discharge. The old Greeks noticed sulphur-like odors accompanying strokes of lightning. Mohr (11) looked up the Homeric songs and found references to these observations in both the Iliad and Odyssey. The smell was most likely due to ozone, and the remarks of Homer are probably the earliest reference to this substance and to reactions initiated by electrical agents.

Activation and chemical reactions. We see from the ancient example just cited that chemical reactions can be produced by enhanced electrical conditions. This fact of observation must necessarily fit into our theories of the nature of chemical reactions if our ideas concerning them are to be of value. We have indeed built up a system of thought concerning chemical activation, initiated by Arrhenius, on the basis of which we can understand the observation of the old Greeks. Certain mixtures of molecules such as the components of air are usually inert and do not react with one another because either one or both of them must be in an abnormal or excited or energy-rich state before they can do so. The reasoning involved is almost naïve. Considering that the substances under discussion can produce a compound by chemical interaction, we say that they have to be brought into a reactive state, because they show no tendency to change while in their ordinary condition. It is painfully obvious that this must be true. The substances must have entered into some other state or condition if we observe that they will undergo chemical changes under the newer situation where we have noticed the chemical reaction to proceed.

One of the simplest ways of increasing the rate of a chemical reaction is to increase the temperature of the system. From such studies it is learned that there is needed a definite amount of energy of activation to cause the chemical reaction to continue. The chemical substances will not change unless the activation energy is available, i.e., unless they are in activated states. It is natural to suppose that other forms of energy applied to chemical systems may produce activation. In this way we have developed the science of photochemistry, where reactions are studied which have been initiated by radiation fields. Similarly any form of electrical discharge produces activated species of molecules and hence may be expected to yield chemical reactions in systems which ordinarily are unreactive.

However, the development of the study of chemical reactions induced in gases and other dielectrics by electrical means followed the path of the physicist in the sense that the discovery and study of various forms of electrical discharge led to their use as agents for the production of chemical phenomena. In many instances the chemical effects noted were at first merely incidental to the course of the investigation. It just happened that the materials changed chemically in the new electrical surroundings.

The chemical changes reported here are produced by any natural or artificial electrical effects whatever in gaseous systems or other dielectrics. The great field of solution chemistry and its component topic of the electrochemistry of solutions are outside of the subject matter of this monograph.

The electrical discharge. Besides the naturally occurring electrical phenomena which cause air, for example, to lose its usual non-conductivity for electricity, there have been developed artificial methods by means of which it is possible to induce new electrical conditions in an otherwise neutral medium. For instance, radioactive materials can induce electrical phenomena in substances placed in their proximity. X-rays similarly can effect conductance in a body they traverse. Flames are found to be highly conducting, and frictional processes can lead to violent electrical discharges in the form of sparks. A most satisfactory method of producing electrical transport and attendant phenomena of light production is the self-sustained electrical discharge. Of the artificial means of electrification of gases the luminous discharge is one of the most convenient methods of producing new electrical conditions.

To trace the history and development of the various forms of the electrical discharge in gases cannot be the province of this monograph. Several authors have dealt with the subject from the point of view of the physicist, for example, Seeliger (1), J. J. and G. P. Thomson (2), Compton and Langmuir (3), Darrow (4) and v. Engel and Steenbeck (5). The physical and electrical phenomena taking place in the electrical discharge have been studied by hundreds of investigators, but still it must be said that no complete understanding of these devices has been attained. Naturally one would like to summarize and portray the background of the physics of the case if one would discuss the chemical effects in electrical discharges. However, the phenomena are of such complex nature that only a very incomplete picture as yet exists and we shall describe the various forms of electrical discharge only in sufficient detail to understand qualitatively the possible chemical actions taking place.

The self-sustained glow discharge. If we consider a glass tube as shown in Fig. 1 with two aluminum discs for electrodes and filled with neon gas at a pressure of 5–10 mm. Hg we will find, upon application of a difference of potential of perhaps a hundred volts, obtained from a battery or a transformer, that there will flow at first an extremely small current due to the natural ionization of the gas produced by cosmic rays, or the accidental presence of radioactive substances, or the existence of powerful electrical fields in the neighborhood of the tube. Shielding and other appropriate means would reduce this effect. If we consider that these precautions have been undertaken and if we increase the voltage applied to the electrodes we would find that at a critical potential the whole tube becomes filled with luminosity and that a comparatively large current will flow through the dilute gas from one electrode to the other. Such tubes are nowadays extremely commonplace; they are the neon signs used extensively for advertising purposes. Under the conditions existing in the electrical discharge, neon atoms are caused to emit red light of high brilliancy which can be seen at great distances.

On closer investigation one notices that the discharge tube under certain conditions is not filled uniformly with radiation. There exist certain dark regions, and at times striations can be produced which follow most remarkable designs. These bright bands of luminosity and the intervening black spaces are of the greatest importance to the behavior of the whole arrangement. Fig. 1 shows a typical assembly. The glow discharge can be divided into the following parts (Fig. 2): (1) the Aston dark space, (2) the cathode glow, (3) the cathode or Crookes dark space, (4) the negative glow, (5) the Faraday dark space, (6) the positive column, (7) the anode glow and (8) the anode dark space. The processes taking place in the discharge are briefly the following: Electrons are liberated at the cathode by either the bombardment of positive ions, molecules of high speed or molecules in a metastable condition, by photoelectric action of radiation or by means of a double layer of atomic dimensions. The favored mechanism

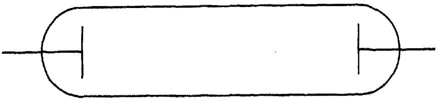


FIG. 1.—Gas discharge tube.

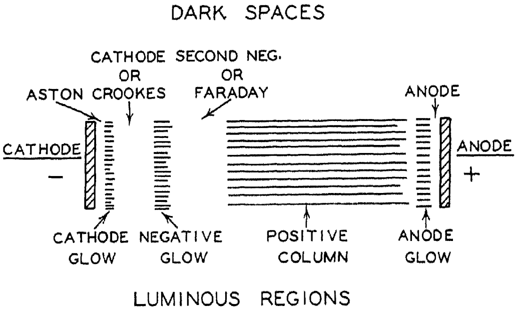


FIG. 2.—Self-sustained luminous discharge.

seems to be the first one mentioned. The electrons freed from the cathode gain kinetic energy as they fall through the field away from it. They can therefore produce more positive ions by impact ionization. The ions eventually reach the cathode, liberating electrons, and as long as this process functions the discharge will maintain itself. It will continue to operate when each electron leaving the cathode will produce enough positive ions so that they in their turn produce one electron at the cathode. The various regions of relative darkness and glow differ in their electrical properties such as potential gradient and space charge due to electrons and positive and negative ions. These particles move in the different sections of the tube with a variety of velocities. Near the cathode we have the Aston dark space where electrons which leave the cathode with little energy gather speed until they are able to excite the gas to luminosity. In the cathode glow we would expect the spectral lines of the gas to appear in the order of their excitation probabilities. Since most of the known excitation functions show a maximum with electron velocity we can realize that, at a distance farther away from the cathode, the electrons will have attained speeds such that they are less likely to cause excitation of the gas. Hence less radiation will be produced in the cathode or Crookes dark space. But these speedier electrons will now have reached sufficient energy to ionize the gas with a concomitant production of new groups of secondary electrons which soon will attain, from the field, enough energy to resonate molecules in their turn. Another region of glow comes into being: the negative glow.

The largest drop in potential occurs in the cathode dark space. In the negative glow the potential is practically constant. The cathode drop is a very characteristic property of the system: electrode metal-gas. It varies with the distance from the cathode in accordance with Aston's law (6).

Let:

$$V = \left(\frac{2V_c}{d^2}\right)\left(dx - \frac{x^2}{2}\right)$$

where V = the potential at x from the cathode; V_c = the total cathode drop; d = the cathode dark space. The gas ions produced and the multitude of electrons created will tend to recombine with emission of radiation. Beyond the region of the large cathode drop smaller forces producing smaller accelerations will act on the electron stream. The electrons will soon lose their ability to resonate. Beyond the negative glow another dark field follows which is called the Faraday dark space. It will extend to the anode in case there are no glass walls confining the discharge. In order that the electrons may reach the anode they will have to attain sufficient speed in the field, and they are again able to cause excitation near the anode, producing the anode glow. If confining walls are present in the vicinity of the region between the Faraday dark space and the anode glow, they will cause indirectly such a field distribution that electrons again can attain sufficient speed for excitation and ionization with the attendant glow of the positive column.

We can see that a great number of possibilities exist for the production by electron impact of all sorts of excited and energy-rich atoms and molecules and that great opportunity is offered in the glow discharge for the appearance of many activated states which can lead toward chemical reaction, impossible had we kept the gas in its normal non-luminous state. It is then no wonder that compound molecules will dissociate and that simple molecules and atoms will enter into new combinations. These possibilities for reaction must be quite different in the various regions of the luminous discharge. Interesting information has been gathered from a detailed study of the chemical effects observed in the different portions. In order to obtain a picture of these chemical processes we need to discuss the types of interaction a molecule may be expected to undergo in such an electrified region as is presented by a glowing column of gas.

Processes in the glow discharge. On the basis of our modern concepts of atomic and molecular structure we would expect the following types of impacts to occur in the electrical discharge:

1. *Elastic impacts* between electrons (E^-) and molecules (M) where neither impact partner suffers a great change in energy and where at most only changes in direction of motion result. These interchanges are of no significance in the production of activated states leading to chemical reaction.

2. *Ionization impacts* represented by

$$E^- \text{ (fast)} + M \rightarrow M^+ + 2E^- \text{ (slow)}$$

resulting in the production of positive ions (M^+) and another electron. The positive ions created will travel towards the cathode if they are produced in a region where a potential gradient exists. If they are formed in a field-free space then they will move about by a process of diffusion depending on their concentration. They are not very efficient in producing further ions by impact with neutral molecules. But such impacts may lead to the formation of clusters, for the field of an ion will create an induced dipole in the neutral molecules if the latter are polarizable. Attractive forces then come into play and clustering takes place:

$$M^+ + M \rightarrow (M \cdot M)^+$$

Upon neutralization of the cluster $(MM)^+$ the whole of the energy of ionization is available and may serve as activation energy for chemical processes as postulated by Lind (7):

$$E^- + (M \cdot M)^+ \rightarrow \text{Products}$$

In the glow discharge which has our immediate attention we have respectable concentrations of positive ions in the negative glow, in the cathode dark space and in the positive column. In the dark space the positive ions move rapidly under the cathode fall of potential, and they may not make as many impacts as they would be expected to make on ordinary kinetic-theory considerations. The greatest concentration of slowly moving positive ions is in the negative glow. Hence, if positive ions are responsible for chemical action, we would look for considerable chemical effect in the negative glow and not so much in the cathode dark space (15–18).

3. *Excitation impacts* of the type

$$E^- \text{ (fast)} + M \rightarrow M^* + E^- \text{ (slow)}$$

whereby the molecule is brought into an excited, energy-rich state. From this higher quantum state (M^*) the molecule will return to the normal condition after a short average life (10^{-7} sec.) with the emission of radiation ($h\nu$):

$$M^* \rightarrow M + h\nu$$

unless the upper quantum state is metastable and then the molecule may live in the activated state for a long time (0.001 sec.). It may transfer its energy to other states, and chemical activation is possible since the intrinsic energy of the excited molecule may become available for the initiation of chemical reaction. Again we find the negative glow the seat of the greatest luminosity, and this region must harbor a large concentration of excited states when compared with the cathode dark space which is relatively non-luminous. So if activated states are responsible for chemical action then we may expect it to a greater extent in the negative glow than in the cathode dark space, and the fact that the negative glow is the most prominent seat of chemical action cannot be used to distinguish between any of the possible mechanisms of chemical change.

4. *Dissociation impacts.* One would not expect direct dissociation by electron impact to occur to any extent. For example, the reaction

$$H_2 \quad 2H, \text{ at } 4.34 \text{ e.v.}$$

has not been observed, although many investigators have looked for the effect. However, the process

$$H_2(^1\Sigma_g^+) \rightarrow H_2(^3\Sigma_u^+) \rightarrow 2H + \text{k.e., at } 11.4 \text{ e.v.}$$

is quite possible. $^1\Sigma_g^+$ represents the normal state of the hydrogen molecule and $^3\Sigma_u^+$ is the antisymmetric state which is unstable (XV, 46). Usually dissociation of complex molecules can occur with ionization in a primary act or as a secondary reaction between the mole ion and neutral molecules. In this manner we can produce CH, CH_2 and CH_3 radicals in a hydrocarbon gas. The existence of CH radical is well established, for the band spectrum of this diatomic molecule has been analyzed and there is satisfactory evidence that "CH" is the carrier of this band spectrum. We must then consider ions, excited and metastable molecules, atoms and radicals as possible agents for the initiation and propagation of chemical reactions. In electrical discharge probably all these agents play a part in the whole reaction complex. In a given case one or the other of these types may predominate. The typical behavior of these reaction species in a glow discharge is shown in Fig. 3.

Dissociation of water vapor in the glow discharge. With this very brief introduction to the physics of the glow discharge as a basis, we will next discuss several typical studies of chemical reactions in such discharge tubes. Of the many researches reported in this field we will cite only certain examples, the particular choices being largely a matter of accident.

The dissociation of water vapor was studied by Linder (8), and the experimental apparatus can be seen in Fig. 4. Two aluminum electrodes E_1 and E_2 can be placed at varying distances by moving a glass tube a within the tube b. Two probe-electrodes m and n were used to investigate the potential situation by measuring the electron densities and energies. m is movable through the magnet L. An electric furnace F permitted baking out of the experimental tube at 350° C. before each run. P is a two-stage mercury vapor pump used to force the decomposition products into the bulb S where they were measured by the MacLeod gauge attached to g. The vessel B supplied water vapor at a rate depending on its temperature. The experimental results of this investigation are shown in Fig. 5. The discharge current was varied from 1 to 28 milliamp. and the electrode spacing from 1 to 9.75 cm. The pressure was 0.75 mm., and the furnace temperature varied from 25 to 50° C. With the pressures and electrode distances used the discharge was abnormal. The negative glow was rose-colored; the positive column and the anode glow were not visible. The separation of the electrodes evidently had little effect on the rate of reaction. Since increasing this separation caused the formation of a longer positive column, whereas the cathode dark space and the negative glow remained practically unaffected, Linder concluded that the dissociation must take place to a large extent in these two last-mentioned regions of discharge.

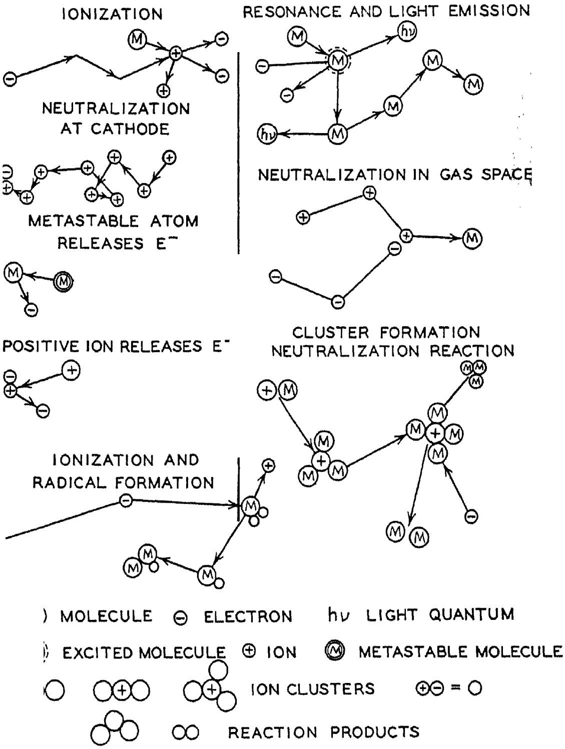

IONIZATION
RESONANCE AND LIGHT EMISSION
NEUTRALIZATION AT CATHODE
NEUTRALIZATION IN GAS SPACE
METASTABLE ATOM RELEASES E⁻
POSITIVE ION RELEASES E⁻
CLUSTER FORMATION NEUTRALIZATION REACTION
IONIZATION AND RADICAL FORMATION
M
hν
MOLECULE
ELECTRON
hν LIGHT QUANTUM
EXCITED MOLECULE
ION
METASTABLE MOLECULE
ION CLUSTERS
⊕⊖ = O
REACTION PRODUCTS

FIG. 3.—Behavior of reactions species in glow discharge.

The gaseous reaction products were hydrogen and oxygen with a small deficiency of the latter from the expected mole ratio 2:1. Perhaps ozone was formed which would not be found by the analytical methods employed. A trace of hydrogen peroxide obtained was insufficient to account for the missing oxygen. The results of the experiments can be presented in terms of the number of water mole

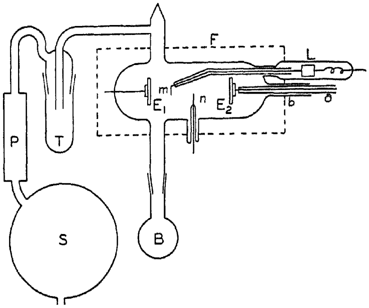


FIG. 4.—Glow discharge tube and auxiliary apparatus used for the decomposition of water vapor. Linder, Phys. Rev. **38**, 679 (1931).

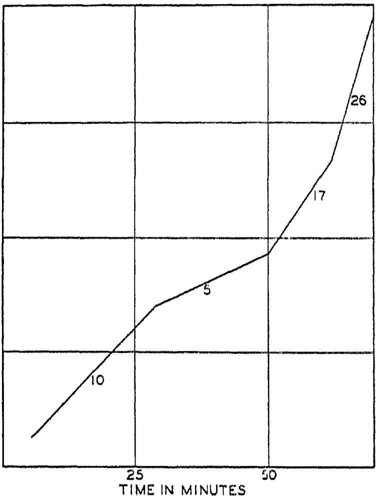


FIG. 5.—Typical curve showing increase of pressure with time for various discharge currents in the decomposition of water. Linder, Phys. Rev. **38**, 679 (1931).

cules dissociating per electron traversing the discharge as shown in column 6 of Table 1.

Energy relations in water dissociation. It is possible to obtain some information regarding the consumption of energy by the electrons of the current while they effected the dissociation of the water vapor. Some of the electrons (n_0) (Fig. 6) will be produced at the cathode ($V = V_1$), and a further number (n_s) will be produced at various places in the dark space. The total energy gained by these two groups will be

$$W = \qquad n_0 e V_1 + \int_{n_0}^{n_1} e(V_1 - V)dn$$

where W = total energy gained by the electrons in the dark space; W_1 = the average energy gained per electron; $n_1 = n_0 + n_s$ = total number of electrons entering the field-free region of the negative glow; V_1 = total cathode drop; $e = 4.774 \times 10^{-10}$ e.s.u., V = potential at any point x.

The average energy of the electron will be less than the calculated amount because of impacts of various kinds. These expenditures cannot be estimated very readily and are not considered in the following calculation. Linder next makes use of an equation of Townsend (9) as modified by Compton and Morse (10):

$$\alpha = pC \cdot exp - \frac{pCD}{X - X'/2pC}$$

where α = number of ionizing collisions made by an electron in advancing 1 cm; p = pressure; C,D = semi-empirical constants of Townsend 12.9 and 22.4, respectively; X,X' = the field strength and its space derivative. When the expressions just given for α and W are united with Aston's law there results a relation for the ratio of electrons crossing the plane at distance x from the cathode to the number of electrons released therefrom (n/n_0). A numerical case is shown in Fig. 6 and in column 5 of Table 1.

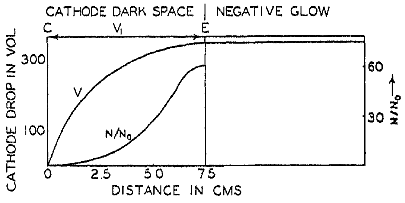


FIG. 6.—Representation of ionization phenomena in Crookes dark space and negative glow. V = cathode drop (volts); n_0 = electrons leaving cathode; n = number of electrons crossing any point.

Linder, Phys. Rev. 38, 679 (1931).

The use of this ratio permits the evaluation of the average energy the electrons have gained when entering the field-free space, barring losses. It is seen (Table 1, columns 5 and 8) that the average energy of the electrons is only about 15% of the whole cathode drop and that the current at the cathode is mostly a stream of positive ions bombarding it. Another point of view is that most electrons originate at the cathode and obtain the full cathode drop. It seems that further studies are needed to elucidate this point.

TABLE 1

ANALYSIS OF RESULTS ON WATER DECOMPOSITION (0.75 MM.) IN GLOW DISCHARGE, BY E. G. LINDER, PHYS. REV. **38**, 679 (1931)

Current (milliamp.)	Dark space, cm.	Cathode drop (volts)	n_1/n_0	Average energy per electron W_1 (volts)	Molecules H_2O decomposed per electron N/n_1	Energy available per dissociation k (volts)	$\frac{V_1 - W_1}{V_1}$ (%)
1	0.96	302	72	53.8	4.78	11.2	82.2
3	0.75	325	59	55.5	5.18	10.7	82.8
5	0.69	343	60	56.8	5.30	10.7	83.1
10	0.61	385	53	63.3	5.67	11.2	83.6
15	0.60	435	63	64.7	6.03	10.7	85.2
20	0.59	500	65	70.5	6.22	11.3	85.9
25	0.56	554	64	79.2	5.90	13.4	85.7

In the neighborhood of the cathode one can write

and

$$\frac{dN}{dt} = \frac{f}{D} W_1 I$$

where N = number of water molecules dissociated by n_1 electrons; D = energy used for dissociation; f = fraction of total electron energy expended in producing dissociation; I = the electron current.

Thus the rate of dissociation and hence of pressure drop is proportional to the current of the discharge *and* the average energy of the electrons. If this relation holds, the available energy D/f should be a constant ($\sim$ 11 e.v.) as is seen from Table 1, column 7. This amount is sufficient to cause the reaction

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 - 2.48 \text{ e.v.}$$

and only the fraction 2.48/11.0 = 0.23 of the total electron energy is used in producing dissociation. The last column of Table 1 shows the energy of the cathode drop not absorbed by electrons and hence must represent the energy of the positive ions. They absorb about 85% of the total amount. This figure checks some direct experimental values obtained by Güntherschulze (12) on water vapor.

Possible reaction mechanisms. In mass-spectroscopic studies (Chapter XVII) it is found that H_2O^+ ion is formed by direct electron impact. Hydrogen atoms and OH^+ ions are produced by subsequent collisions with any molecule M:

$$H_2O^+ + M \rightarrow H + OH^+ + M$$

But other structures also have been noted such as O^+ ions and negatively charged particles. The oxygen ion may result from

$$OH^+ + M \rightarrow H + O^+ + M$$

The subsequent recombination of hydrogen and oxygen atoms or ions will then produce the products of decomposition. Or the process may be brought about by the clustering mechanism of Lind (7):

$$H_2O^+ + H_2O \rightarrow (H_2O \cdot H_2O)^+; \ (H_2O \cdot H_2O)^+ + E^- \rightarrow 2H_2 + O_2$$

However, Linder (8) remarks that it does seem unlikely that all the dissociation observed can be ascribed to ionization since this would require a very large ionizing power for the electrons. The number of ions produced per electron of W_1 volts of energy would then be about five (Table 1), which is several fold the ionizing power usually observed (Compton and Langmuir [3]). Hence he supposes that some excited molecules take part in the reaction and dissociate:

$$H_2O^* + M \rightarrow H_2 + \tfrac{1}{2}O_2 + M$$

The resonance potential of the water molecule has been reported at 7.0 e.v. (13), which is sufficient energy to cause the reactions

$$H_2O^* \rightarrow H + OH + 2.00 \text{ e.v.}; \quad H_2O^* \rightarrow H_2 + O + 2.00 \text{ e.v.}$$

The first of these seems more likely since the spectrum of a water discharge (14) shows the Balmer lines and the OH bands strongly and the molecular spectrum of hydrogen (H_2) is not prominent.

However, the clustering mechanism may be

$$H_2O^+ + 4H_2O \rightarrow (H_2O)_5^+; \quad (H_2O)_5^{+} \quad e^- \rightarrow 5H_2 \quad \tfrac{5}{2}O_2$$

and five water molecules are decomposed per ion formed. The energy relations are satisfied, for the ionization potential of the water molecule is 13.0 e.v. and the energy required for the dissociation of five water molecules is 5 × 2.5 = 12.5 e.v. In the discharge the electron expends W_1 volts of energy (Table 1), which is about five times the amount needed to produce a water ion. The difference must go into physical processes of light production, heat, etc.

Water formation in glow discharge. Güntherschulze (12) found that the cathode drop in gas mixtures was proportional in some cases to the concentration of the molecules in accordance with a simple arithmetical rule for mixing. Such a pair of gases is mercury and argon, and the relation between the cathode drop of their mixture and the composition is shown in Fig. 7. On the other hand it appeared that this simple relation did not hold at all for gas mixtures which showed chemical activity in glow discharge. These reactive mixtures have an excess cathode drop over the amount expected from the mixture, and Güntherschulze thought that this excess must be used in performing the chemical action in the discharge. He considered that the excess voltage gives the electrons the extra energy needed for the production of chemical changes. In water formation it is found that

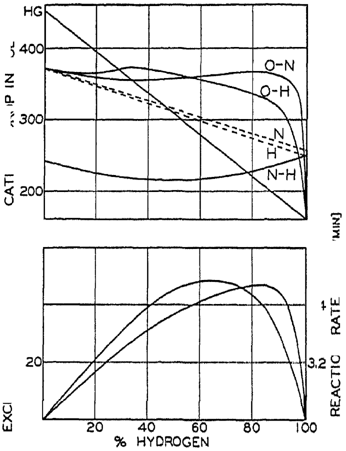


FIG. 7. Water synthesis in glow discharge. Excess cathode drop and reaction rate as a function of composition. Güntherschulze, Z. Elektrochem. 30, 386 (1924).

increased hydrogen concentration is favorable toward a larger reaction rate, and hence it appears that the hydrogen molecules are the species being ionized in glow discharge, rather than the oxygen molecules. An electron needs 17.86 e.v. for the dissociation and ionization of a hydrogen molecule:

$$\begin{array}{ll} H_2 \rightarrow 2H, & -\ 4.34 \text{ e.v.} \\ H \rightarrow H^+ + E^-, & -\ 13.52 \text{ e.v.} \\ \hline H_2 \rightarrow H + H^+ + E^-, & -\ 17.86 \text{ e.v.} \end{array}$$

Water synthesis was found to be directly proportional to the current and independent of the gas pressure. If then a current of 50 milliamp. is thought to consist of electrons entirely, at least in the negative glow, then 1.89×10^{19} electrons will pass down the discharge. Each one of them needs 17.86 e.v. of energy for the dissociation of a hydrogen molecule. If the excess cathode drop (V) represents the available energy which the electron can use for such acts, then the number of hydrogen atoms formed will be

$$\frac{2 \times 1.89 \times 10^{19} \times V \times e}{17.86\, e} = 2.1\, V \times 10^{18} \text{ atoms}$$

One cubic centimeter of electrolytic gas contains 1.67×10^{19} molecules at 20° C. and 760 mm. pressure. If each hydrogen forms a water molecule then a current of 50 milliamp. will use up 0.1316 V cc. of gas. The calculated and observed reaction rates check quite well for gas mixtures containing from 20 to 80% hydrogen. The excess cathode drop is about 10% of the whole. In other words, the electrons use about 10% of their total energy for chemical reaction. Or might it be that they have on the average this amount of energy on entering the negative glow as Linder (Table 1) would calculate? The considerations just presented do not apply to nitrogen-hydrogen mixtures, for in them the cathode drop excess is negative. Hence these two gases should not react in the glow discharge, and Güntherschulze does not find a pressure change at ordinary temperatures. Under these conditions the decomposition of any ammonia formed proceeds at once, and the total effect is no apparent reaction. However, ammonia can be synthesized in glow discharge, as will be seen from the work of Brewer et al. (15–18), if one takes care to remove the ammonia once formed from the seat of the discharge (page 20). The proposed hypothesis that the excess cathode drop is important in regard to the energy considerations pertaining to the chemical reactions in glow discharge does not complete the picture, and further studies are needed.

Another interesting observation made by Güntherschulze is very suggestive. Helium-oxygen and argon-oxygen mixtures also show deviations from the linear relation of cathode drop and composition. A positive excess cathode drop is found. Does this situation indicate that chemical interaction takes place between oxygen and these rare gases? One would expect that such chemical action might, if at all, happen in glow discharge where excited and ionic states of the rare gases exist. If the rare gases ever have chemical properties then they must be due to their excited states, as in the well-known case of helium molecule (He_2).

Ammonia synthesis in glow discharge. In a series of investigations Brewer and co-workers (15–18) have lately studied a variety of chemical reactions in the glow discharge. Of these researches we will discuss only a few in order to bring out the main features of such reactions. Two of the experimental set-ups used by these investigators are shown in Figs. 8 and 9. The electrodes were usually aluminum, which does not sputter appreciably. The pressures used varied from 3 or 4 mm. Hg to about 0.1 mm. Part or all of the reaction vessel was immersed in liquid air, so that the reaction products were frozen out on the walls of the discharge tube. The variables—pressure, current, effect of external magnetic fields, and shape of discharge tube—were studied as to their influence on the chemical reaction.

Pressure and temperature have no influence on the synthesis of ammonia in the glow discharge from a $3H_2:N_2$ mixture.

Influence of current. However, the rate of synthesis is dependent on the total discharge current and is in fact proportional to it:

$$dP \qquad \alpha I$$

where dP/dt = rate of pressure drop; α = proportionality constant; I = current. The relation can best be seen from Figs. 10, 11 and 12. The proportionality constant depends on the size and shape of the reaction vessel and upon the direction and intensity of the external magnetic field when applied. For a particular tube it is independent of the pressure and potential gradient of the discharge. The proportionality between current and reaction rate is obtained with all types of reaction vessels. For example, the experiment represented by curve 6 (Fig. 11) was carried out in a long spiral glass tube of small bore, in which the pressure varied from 0.7 to 0.05 mm. Hg. It would be expected that the pressure drop observed would refer to the net result of synthesis and decomposition of ammonia, for it is known that charged particles reach the confining walls of a discharge where the reaction product accumulates. This situation was observed in the U-shaped reaction tube shown in Fig. 8. The results obtained are

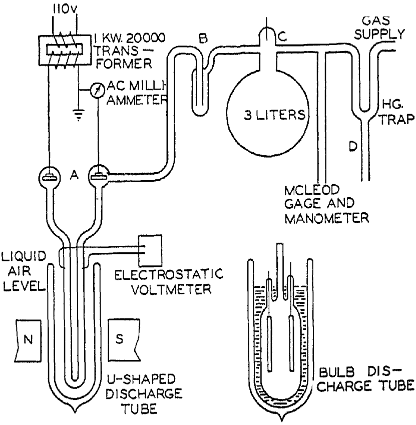

110V
1 KW. 20000 TRANS-FORMER
AC MILLI AMMETER
B
C
GAS SUPPLY
3 LITERS
HG. TRAP
D
A
MCLEOD GAGE AND MANOMETER
LIQUID AIR LEVEL
ELECTROSTATIC VOLTMETER
N
S
U-SHAPED DISCHARGE TUBE
BULB DIS-CHARGE TUBE

FIG. 8.—Experimental arrangement for ammonia synthesis. Brewer and Westhaver, J. Phys. Chem. 33, 883 (1929).

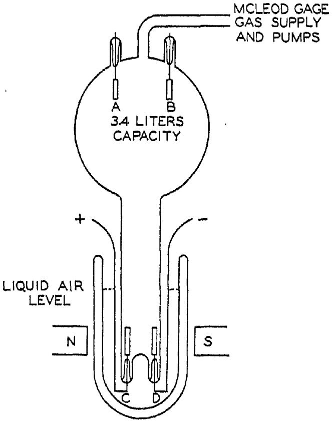
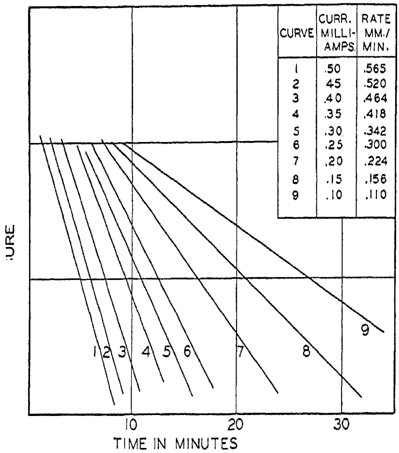

MCLEOD GAGE
GAS SUPPLY
AND PUMPS
A
B
34 LITERS
CAPACITY
+
-
LIQUID AIR LEVEL
N
S
C
D

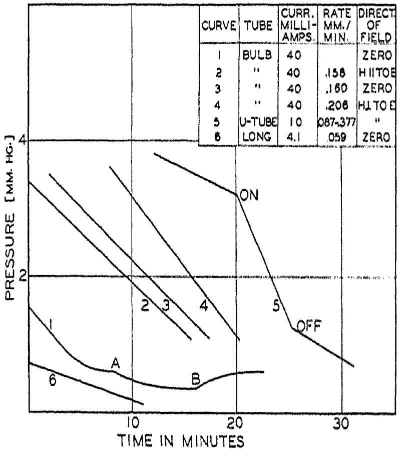
FIG. 9.—Discharge tube permitting diffusion of gases. Used in ammonia synthesis. Brewer and Westhaver, J. Phys. Chem. 34, 153 (1930).

recorded in curve 1 of Fig. 11. With a current of 40 milliamp. the reaction stopped at point *A* where a steady state was reached. At 15 milliamp. further synthesis could be obtained (*A* to *B*), but increasing



CURVE	CURR. MILLI-AMPS.	RATE MM./MIN.
1	.50	.565
2	.45	.520
3	.40	.464
4	.35	.418
5	.30	.342
6	.25	.300
7	.20	.224
8	.15	.156
9	.10	.110

FIG. 10.—Pressure changes in discharge tube during ammonia synthesis for various currents. Brewer and Westhaver, J. Phys. Chem. 33, 883 (1929).



CURVE	TUBE	CURR. MILLI-AMPS.	RATE MM./MIN.	DIRECT OF FIELD
1	BULB	40		ZERO
2	"	40	.158	H ‖ TO E
3	"	40	.160	ZERO
4	"	40	.208	H ⊥ TO E
5	U-TUBE	10	087-.377	"
6	LONG	4.1	.059	ZERO

FIG. 11.—Pressure changes in discharge tube during ammonia synthesis, showing effect of magnetic field. Brewer and Westhaver, J. Phys. Chem. 33, 883 (1929).

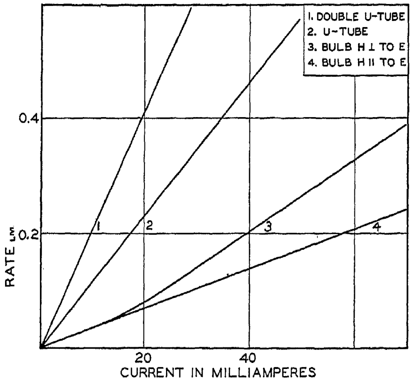


FIG. 12.—Rate of synthesis of ammonia as a function of current. Brewer and Westhaver, J. Phys. Chem. **33**, 883 (1929).

the current again to its former value also brought back the former equilibrium pressure.

Effect of magnetic field. An external magnetic field has a twofold effect on the character of the glow discharge. The glow becomes concentrated into definite sheets and bands, and, when the field is applied perpendicular to the original motion of the electrons, it becomes necessary to increase the potential needed to maintain the discharge. The glow in the U-tube concentrates into two narrow bands farthest removed from the magnet pole pieces, rather than being located in the center of the tube as is the case without an external field. For the bulb, with the field parallel to the plane of the electrodes, the glow was confined to a single sheet, and with the field perpendicular to the plane of the electrodes two sheets were formed, one passing through either electrode parallel to the field. Curve 5 (Fig. 11) shows the effect of a perpendicular field of about 1000 gauss. The rate increases from 0.087 to 0.377 mm. per min., and the potential drop on the probe-wires was increased from 3200 to 4400 volts. It should be noted that the parallel field had no effect on the rate of synthesis.

Other factors. An external electric field had no appreciable effect. The length of the positive column immersed in liquid air was a definite factor affecting the rate. The longer the positive column immersed, the higher was the rate (Fig. 12). The power consumption was calculated as the product of current and potential.

Seat of reaction in glow discharge. In a discharge tube 2 cm. in diameter and 70 cm. long which could be immersed to a distance of

60 cm. in liquid air Brewer and Westhaver (15) showed that ammonia synthesis occurred only in the luminous discharges such as the negative glow and the positive column and not in the Crookes and Faraday dark spaces. The situation is shown in Fig. 13. The negative glow is by far the most prominent region for synthesis. It is also the seat of the greatest concentration of positive ions, and from it comes the most intense radiation.

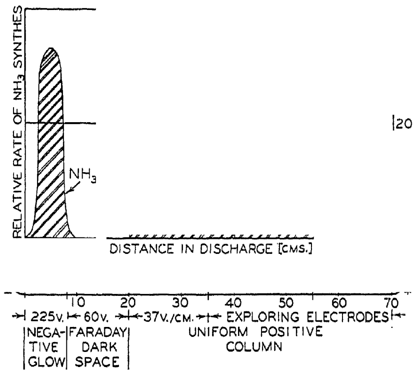


FIG. 13.—Seat of ammonia synthesis in glow discharge. Brewer and Westhaver, J. Phys. Chem. 34, 153 (1930).

In interpreting these results, Brewer however has a different picture of the discharge from that due to Linder (page 11). Linder assumed that most of the current at the cathode was a positive ion current and electrons made impacts in the dark space, producing more positive ions; which, however, caused little reaction, perhaps because of their speed. Brewer, on the other hand, believes that the current at the cathode is essentially a stream of electrons. They are produced at the cathode largely by impacts of metastable atoms. When they enter the dark space, they make *no* impacts there because their mean free path is greater than the extent of this region. The electrons attain therefore the full cathode drop before they make collisions in the negative glow. If one recalls the information obtained by physicists (1–5) on the pertinent questions of the agents producing electrons at the cathode, then one sees that the physics of the problem has not been worked out completely. It is not a settled question whether ions or metastable molecules or both are responsible for the emission of the cathode electrons. Hence the detailed mechanism of chemical reactions in glow discharge must await the findings of the physicists before a definite answer can be given.

Effect of added gases. While ammonia synthesis was usually studied with the $3H_2:N_2$ mixture, the effect of excess of either constituent and also the addition of helium or argon were examined by Brewer and Westhaver (15). The rate of reaction is independent of the pressure as long as the composition of the gas does not change. The maximum rate of synthesis was obtained at approximately a $2H_2:N_2$ mixture rather than with a $3H_2:N_2$ composition, as is seen from Fig. 14. The portions of this curve on either side of the maximum show a ratio

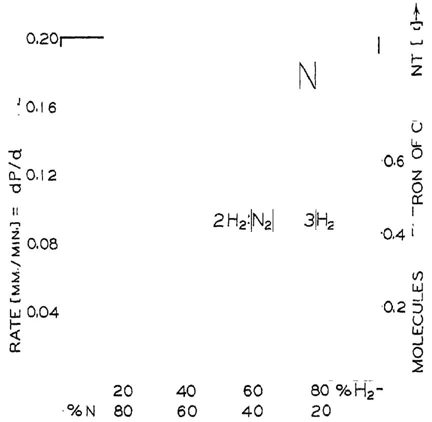


Fig. 14.—Rate of ammonia synthesis for various hydrogen-nitrogen mixtures. Current = 40 milliamp.; magnetic field through discharge; rates measured at 3.5 mm. Hg pressure. Brewer and Westhaver, J. Phys. Chem. 34, 153 (1930).

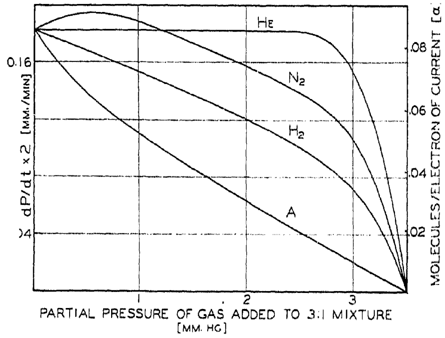


Fig. 15.—Effect of added gases on rate of synthesis of ammonia in glow discharge. Current = 40 milliamp.; magnetic field through discharge; rates measured at 3.5 mm. Hg pressure. Brewer and Westhaver, J. Phys. Chem. 34, 153 (1930).

of slopes of about 3:1. This indicates that in hydrogen-rich mixtures addition of nitrogen has three times the effect of a similar addition of hydrogen to nitrogen rich mixtures. The influence of helium and argon is shown in Fig. 15. Helium does not change the reaction rate up to 70% of the total quantity of gas present, but argon affects the synthesis in a very pronounced manner.

Effect of cathode material. In Chapter XIX, where we will discuss the phenomenon of cathodic sputtering, it will be seen that a very definite chemical reaction can occur in a glow discharge between the cathode metal and the gas carrying the discharge. This interaction will be prominent whenever the metals, such as arsenic, antimony and bismuth can form definite chemical compounds in hydrogen. In these instances, so-called chemical sputtering is known to take place. However, it is conceivable that the nature of the cathode metal will have an effect on chemical reactions in glow discharge simply by reason of the fact that the cathode drop varies for different metals in the same gas. Kueck and Brewer (18) have studied this point by investigating ammonia and water synthesis with a variety of different metals as cathode. They found that the rates of these syntheses in the negative glow are in general directly proportional to the normal cathode fall of potential of the various metals. The change in cathode drop due to pressure has no effect on the rate of reaction. Deviations from proportionality are small in water synthesis, but in the ammonia reaction they are quite large, although the general trend is definite. The relation found between rate of synthesis and cathode drop is interpreted to indicate an increase of positive ion production with increased acceleration of the electrons. The variations from one surface to another are thought to be due to the change in ratio of positive to electron current.

Reaction mechanism. Brewer and Westhaver (15) consider positive ions, excited molecules and neutral atoms as possible agents in ammonia synthesis. The outstanding features of the experiments in glow discharge are that the reaction is directly proportional to the discharge current and that it is independent of pressure over a large range of values. The last-mentioned observation seems to exclude the possibility that the mechanism involves any complex system of formation and dissociation of particles since any such process would be pressure sensitive. It seems improbable that any sort of equilibrium situation should not be affected by current density, diameter of the reaction tube, pressure and temperature of the gas, position in discharge where the chemical change takes place and different magnetic and electrostatic fields. It appears that the synthesis must be due to one single mechanism operative under all conditions. They favor an ionic reaction, since the production of ions and hence their concentration may be expected to increase proportionally to the current, as does the rate of synthesis. If excited molecules were responsible the reaction should be pressure sensitive, for it may be expected that the concentration of excited molecules would decrease with pressure. The spectrum of the discharge changed completely during a single experiment, a pure band spectrum being obtained at high pressures, while the emission consisted almost entirely of lines at low pressures. Brewer and Westhaver further cite their observations in a magnetic field in support of an ionic mechanism. The general glow throughout the tube, and by implication the concentration of excited molecules, was eliminated by an application of a magnetic field parallel to the plane of the electrodes. This situation had no effect on the current or on the rate of synthesis. The magnetic field perpendicular to the plane of the electrodes, though again eliminating the general glow, increased the number of electrons and positive ions and also increased the rate of synthesis. On the other hand, neutral atoms would increase in concentration at lower pressures if produced by dissociation. If they were involved in the reaction one would expect an increased rate at lower pressures. Furthermore, Crew and Hulbert (19) have shown that the concentration of nitrogen atoms is very low in the type of discharge used in these experiments and that the number of hydrogen atoms varies markedly with pressure. In further support of their arguments, Brewer and Westhaver cite the experiments of Kunsman (Chapter IX) and Storch and Olson (Chapter V), who studied ammonia synthesis with electrons of controlled speed. No reaction was obtained below the ionization potential of the gas. On the other hand, Lewis (Chapter XII) believes that he has evidence for an atomic mechanism of ammonia synthesis.

The results obtained from the various hydrogen-nitrogen mixtures indicate according to Brewer and Westhaver that nitrogen ions are much more efficient as agents for reaction than are hydrogen ions. The various ions are produced in accordance with the intrinsic probability of ionization by electron impact (3) and depend also in a given mixture on the relative concentration of the molecules concerned. The chances of ionization of nitrogen and of hydrogen are 8.72 and 2.84, respectively, on the basis of the stopping power of helium being unity.

Consequently one would expect

$$\frac{N_2^+}{H_2^+} = \frac{8.72 \times 1}{2.84 \times 3} = \frac{1.02}{1.00}$$

in a $3H_2:N_2$ mixture, and similarly

$$\frac{N_2^+}{H_2^+} = \frac{8.72 \times 1}{2.84 \times 2} = \frac{1.5}{1.0}$$

in a $2H_2:N_2$ mixture. Since maximum reaction is observed in the last-mentioned gas, it follows that nitrogen mole ions are more efficient in producing synthesis than hydrogen mole ions. The effect of the rare gases helium and argon on the rate of ammonia synthesis shows that helium does not interfere with the relative production of nitrogen and hydrogen mole ions, whereas argon, which has about the same ionization potential (15.7 e.v.) as nitrogen (15.65 e.v.) and hydrogen (15.9 e.v.), would have a definite effect by virtue of energy exchange. With older values of the ionization potentials of nitrogen (16.8 e.v.) and hydrogen (15.3 e.v.), Brewer and Westhaver argued that the behavior of argon indicated that nitrogen mole ions are of primary importance. But the latest values of the ionization potentials could now perhaps be used to demonstrate that hydrogen mole ions are more probably responsible for the reaction mechanism.

Electrochemical equivalence law (IX). The fact that the rate of ammonia synthesis is proportional to the discharge current led Brewer and Westhaver (15) to adopt an electrochemical equivalence law similar to the laws of Faraday established for the electrochemistry of solutions:

$$\genfrac{}{}{0pt}{}{}{dt} = \alpha I$$

However, we have seen that others, for example Linder, assume the rate of reaction to be proportional not only to the current but also to the energy of the impinging electrons. In spite of the great simplicity found experimentally in the behavior of these reactions as far as proportionality to the current and independence of pressure are concerned, it must be said that the detailed mechanism appears to be one of extraordinary complexity.

Various reactions and M/N ratios. Brewer and co-workers (15–18) studied the following reactions in glow discharge: $N_2 + 2O_2 \rightarrow 2NO_2$; $3O_2 \rightarrow 2O_3$; $2H_2 + O_2 \rightarrow 2H_2O$; $2CO + O_2 \rightarrow 2CO_2$; $2CH_4 \rightarrow C_2H_4 + 2H_2$; $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$; $2N_2O \rightarrow 2N_2 + O_2$; $2NO_2 \rightarrow N_2 + 2O_2$. For all these reactions they assume an ionic mechanism, and they evaluate ratios (M/N) of molecules reacting (M) per ion pair (N) as found by Lind (7). The electrochemical equivalence law is said to hold, and the general behavior is that outlined in detail for ammonia formation. Explosion in water synthesis and in carbon monoxide oxidation, i.e., chain propagation of reaction, is found only in the positive column.

Hydrocarbons in glow discharge. A great variety of these substances have been studied in all forms of electrical discharge. The simplest reaction has been observed in methane by Brewer and Kueck (17), who found that the gas decomposes into ethylene in glow discharge if the whole reaction tube is placed in a liquid air bath (Fig. 16). The reaction is

$$2CH_4 \rightarrow C_2H_4 + 2H_2$$

It appears that this step is the primary act, for much more complicated products are obtained when the decomposition is carried out at higher temperatures such as room temperature, for then solid products are obtained by further action on the ethylene produced. In the arrangement used by Brewer and Kueck the first product formed (ethylene) is removed from the seat of the discharge by freezing out at the walls of the tube which are at liquid-air temperature. Harkins and Jackson (20), on the other hand, studied methane decomposition in the glow discharge at ordinary temperatures and obtained a solid material in the form of a thin film of the composition $(C_{1.00}H_{1.25})_n$. Similarly Linder (21) and Linder and Davis (22) while studying a series of fifty-seven hydrocarbons found among the reaction products a waxlike, inert substance deposited largely on the cathode. They used an apparatus very similar to the one already shown in Fig. 4. The gaseous products obtained were hydrogen, acetylenes, ethylenes and paraffin hydrocarbons. The rate of decomposition (Fig. 17) was found to be constant for a given current and increased proportionally with larger currents. The solid products formed decreased with increase in the hydrogen-carbon ratio of the hydrocarbon studied. The rate of gas evolution followed two empirical rules: (1) In a series of similar compounds (e.g., paraffins) the rate of gas evolution increases with molecular

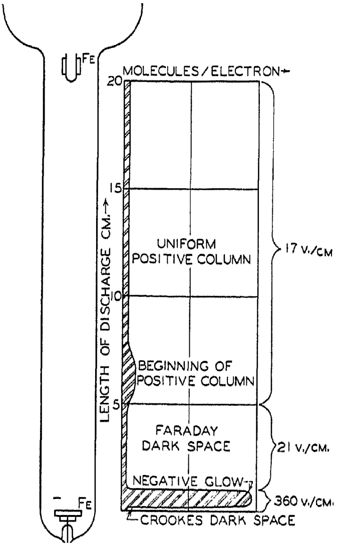


FIG. 16.—Decomposition of methane in luminous discharge. Reaction tube immersed in liquid air. Brewer and Kueck, J. Phys. Chem. 35, 1293 (1931).

weight. (2) In a series of similar compounds of the same molecular weight (e.g., ortho-, meta-, para-xylene) the rate of gas evolution increases with decreasing centralization. Linder and Davis found a striking parallelism between the rate of gas production and the

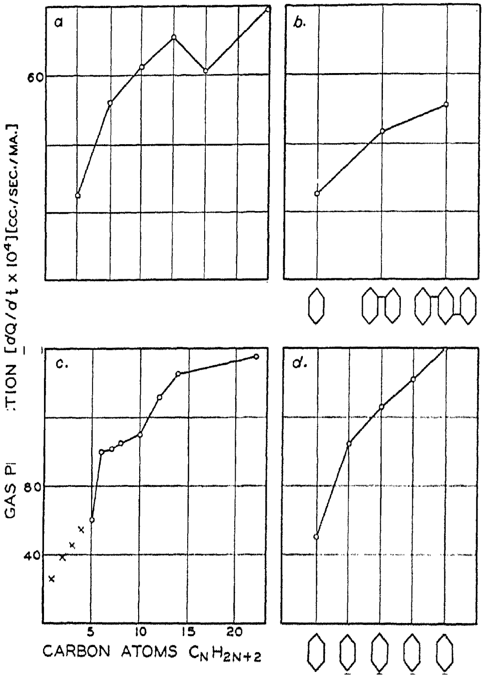


FIG. 17.—Rates of gas production for hydrocarbons in glow discharge. (*a*) Methyl-substituted benzene series: benzene, toluene, paraxylene, mesitylene, durene, and hexamethylbenzene. (*b*) Benzene, diphenyl and paradiphenylbenzene. (*c*) The normal hydrocarbons. (*d*) Monosubstituted benzene series: benzene, toluene, ethyl benzene, normal propyl benzene, and normal butylbenzene. Linder and Davis, J. Phys. Chem. 35, 3649 (1931).

knock-rating of Lovell, Campbell and Boyd (23). The latter state that "in a homologous series the tendency to knock increases with increasing length of the carbon chain and in an isomeric series the tendency to knock usually decreases as the number of side chains is increased." This behavior of hydrocarbons in a combustion engine goes parallel to their decomposition in the glow discharge. The former authors adopt the usual view that the chemical reaction observed is due to ions and excited molecules. They suggest that hydrocarbon molecules of increasing complexity should have a more complicated set of quantum levels or states and hence should show greater ease of excitation as compared to ionization. The total rate of decomposition in the discharge will be given by an equation of the form

$$\frac{dg}{dt} = aN + bM^*$$

where dg/dt = rate of gas evolution; a, b = constants; N = rate of formation of ions; M^* = rate of formation of excited molecules. The rate of reaction per ion can then be written

$$\frac{dg}{dt \cdot N} = a + b(M^*/N)$$

and it is seen that it should increase when the ratio (M^*/N) increases. If larger molecules are more readily excited than ionized, then the observed effects can be understood. Larger molecules also may be ionized more readily because their probability of ionization may be greater, owing to greater complexity, and they may show increased reactivity on that account. Since neither excitation nor ionization functions are known for the hydrocarbons under discussion, no decision can be made as to the mechanism of reaction. A further interesting observation made in this investigation is the possible additivity of the rates of gas evolution. The points marked by crosses on Fig. 17 have been obtained by subtracting the rate of benzene from that of toluene, ethylbenzene, normal propylbenzene or normal butylbenzene. The values so calculated lie on the normal paraffin curve.

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CHAPTER II

CHEMICAL REACTION IN SILENT ELECTRICAL DISCHARGE

The silent electrical discharges. We have seen how the luminous discharge can maintain itself by processes of ionization and electron emission at the cathode. The various glowing and dark regions can readily be distinguished at low enough gas pressure. Their existence can be understood at least to some extent although a great deal of further information must be obtained before we have a complete picture of the physics of the glow discharge. Other forms of discharge which operate at higher pressure (about one atmosphere) have been used for chemical investigations such as the point discharge, the corona discharge and the silent electric discharge as produced in an ozonizer. These three forms of discharge are closely related to the glow discharge in the sense that the electrical phenomena taking place in them are essentially the same. The differences are due to the higher pressure employed in these devices. It is known that near the curved surface of a point the field will be abnormally high, creating the possibility of ionization in close proximity to the point. This fact brings about a more complex condition such that the various regions are not so readily distinguishable.

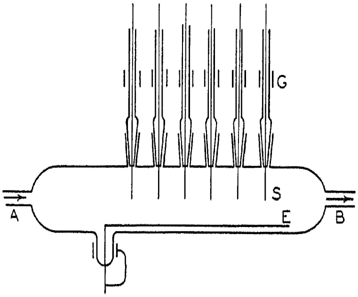

FIG. 18.—Point discharge apparatus for production of ozone. S = point electrodes; E = plate electrode; g = guard electrodes; A = gas entrance; B = exit for reaction products. Warburg, Ann. Physik 17, 1 (1905).

Point-plate discharge. If a point discharge is considered as shown in Fig. 18, and if the point electrodes are negatively charged and hence serve as cathodes then there are developed about them the usual cathode dark space and negative glow. These regions can be distinguished only under the microscope, but they become visible to the naked eye as the pressure is lowered. Depending on the distance "point plate," a positive column may or may not be developed. When the point serves as anode and is then positively charged, one sees again at high pressure a glowing region near it which easily goes over into a brush discharge formed by the positive column. From this brief description of the point plate discharge one would deduce that the negative point discharge with its well-developed negative glow would show greater chemical activity than the positive point discharge, since it is recalled that the greatest chemical action in luminous discharge was found in the cathode glow.

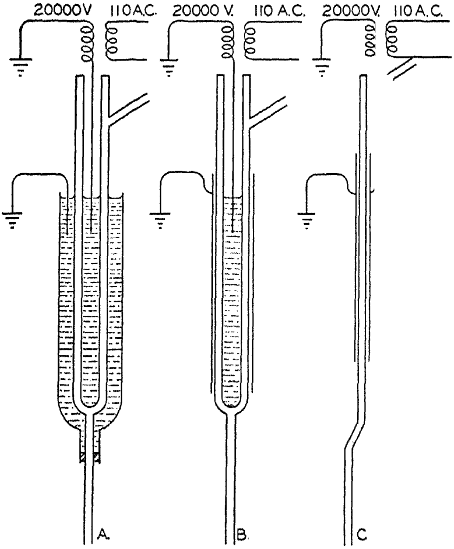

FIG. 19.--All-glass ozonizers: cylindrical type: (*a*) two water electrodes; (*b*) metal outer and water inner electrode; (*c*) two metal electrodes.

Ozonizers. The ozonizers shown in Figs. 19–22 have been used by many investigators for the purpose of studying chemical reactions. The very name, of course, suggests that they have served for the preparation of ozone from oxygen. This particular reaction has been investigated to such an extent that two special monographs have been written by Moeller (1) and Rideal (3) concerning it. Warburg (2) and Berthelot (4) have carried out a great number of reactions by means of the silent electric discharge obtained in an ozonizer. The original form of this type of discharge tube was first used by Siemens (5).

Since then most investigators have made some minor changes in design without, however, affecting the type of discharge obtained. Perhaps the most important improvement was made by Frölich (6), who built the inner electrode of metal as shown in Fig. 22. These devices are to be considered as a system of condensers, and the type of discharge obtained in the annular gas space between the two glass tubes or the glass and metal tubes is of the form of a positive and negative point discharge. The discharge as a whole consists really of a series of brush discharges which increase in number as the current density increases, when the whole annular space appears to be filled with luminosity. Alternating current is employed, since in this case the necessary charging of electrodes occurs which makes the production of a current in the gas space possible. Since the current in ozonizers is produced and carried by positive and negative point discharges, we may expect the chemical action to be the same as in the point-plate discharge.

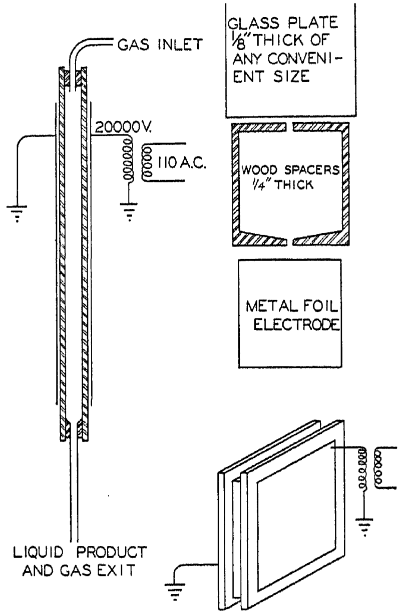
GAS INLET
20000V.
110 A.C.
LIQUID PRODUCT AND GAS EXIT
GLASS PLATE 1/8" THICK OF ANY CONVENIENT SIZE
WOOD SPACERS 1/4" THICK
METAL FOIL ELECTRODE

FIG. 20.—All-glass ozonizers, plate type. Single unit.

Ozone formation in point-plate discharge. The apparatus shown in Fig. 18 was employed by Warburg (2) in a study of ozone formation by a point discharge. Oxygen gas was allowed to flow past the discharge points, and the exit gas was analyzed for ozone. Since the resulting product is also decomposed by the electrical discharge the results are given extrapolated to zero concentration of ozone (A_0). If m grams of ozone were formed in t hours with a current of J amperes then the yield is $A = m/(Jt)$. In Table 2 the results are given for experiments conducted at 760 mm. pressure and room temperature. The fourth column gives the number of coulombs of electricity needed for the production of one equivalent of ozone. It is seen that various amounts of electricity are necessary for one equivalent (24 grams) of ozone, depending on the conditions. These results indicate that the processes of formation of ozone in the point discharge are not of the type of an electrolysis where Faraday's laws hold. It must be stated, however, that these experiments are not carried out under such simple reproducible conditions as are possible in the electrolysis of solutions.

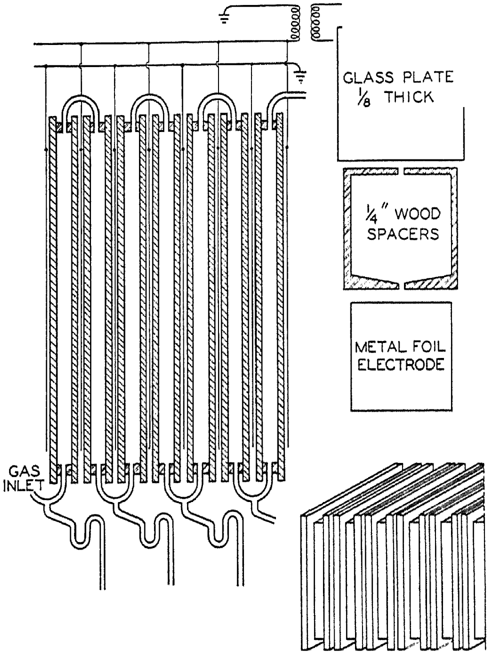

FIG. 21.—All-glass ozonizer; plate type. Multiple unit.

However, the number of coulombs needed in the various experiments cited vary from 84 to 1400 per equivalent, and it seems difficult to believe that uniform experimental conditions can be discovered such that Faraday's laws could be expected to apply (IX).

When we recall the chemical studies made in the glow discharge at low pressure, we would expect the negative point discharge to show the greater chemical activity. This condition seems to exist if one notes the first two experiments given in Table 2. However, when the positive point discharge includes a brush discharge (positive column) then the combined yield is larger (Expts. 3, 4 and 5, Table 2). For comparison two experiments made in ozonizers are included in the table which show that these types of apparatus are much more efficient for the production of ozone in spite of the smaller currents they carry.

For the negative point discharge it can be shown that the chemical reaction takes place in the luminous portion around the negatively charged wire, for the yield is constant as long as the current remains at a given value, even though the distance point-plate and the potential be increased. We are reminded of similar experiments carried out by Linder (Table 1) on the decomposition of water vapor in the luminous discharge where the electrode distance had only a small effect on the reaction.

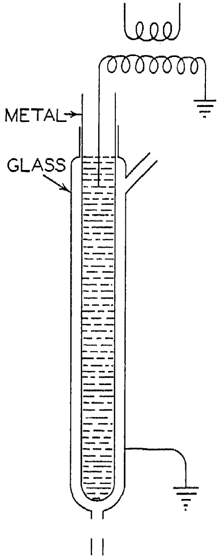

FIG. 22.—Metal-glass ozonizer. Inner electrode metal, outer one glass.

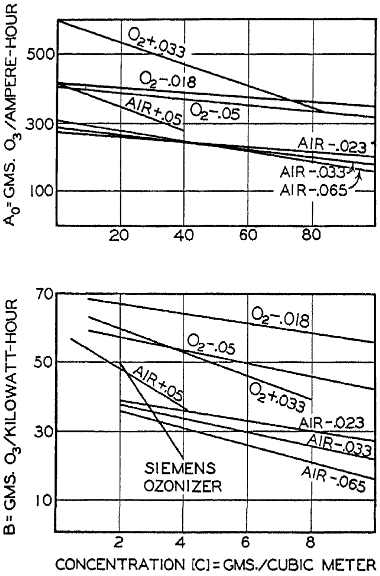

FIG. 23.—Formation of ozone in point discharge in oxygen and air from positive and negatively charged spherical points as function of ozone concentration at various current densities. Warburg and Leithäuser, Ann. Physik **20**, 734 (1906).

The results of similar investigations by Warburg and Leithäuser (7) are summarized in Fig. 23 where the yield A_0 gives the number of grams of ozone formed per ampere-hour from either air or oxygen and

TABLE 2

OZONE FORMATION IN A POINT DISCHARGE
E. Warburg, Jahrb. Radioakt. Elektronik 6, 202 (1909)

Type of Discharge	Current $J \times 10^6$ (amperes)	Yield $A_0 = \frac{m}{Jt}$	Coulombs per gram-eq. Ozone (24)
Positive point discharge	28.8	61.8	1398
Negative point discharge	17.4	174.0	497
Positive point brush discharge, electrode distance 4 mm; wire 1-mm diameter drawn to a point	42.5	313	276
Negative point discharge, electrode distance 1 cm; spherical point electrode*	17.5	419	206
Positive point discharge, brush discharge, electrode distance 1 cm; spherical point electrode	33.0	598	144
For comparison:			
All glass ozonizer, gas space 3.7 mm	0.085†	889	97
Metal-glass ozonizer, gas space 4.66 mm	0.187†	1033	84

* Spherical points are better than drawn ones.
† Amperes per square meter.

from positive and negative point discharges. B is the technical yield in grams of ozone per kilowatt-hour. Other features of reactions in the point discharge find their equivalent in the luminous discharge, the ozonizer and the corona, and need not be dealt with in detail, for the other forms of electrical discharge are more satisfactory means of studying chemical reactions in electrified gases. Future investigations most likely will not be carried out in the form of discharge just discussed, if their object is the elucidation of reactions with the electrical mode of activation.

Potential distribution in an ozonizer. Warburg (2) has made the most extensive studies of the behavior of ozonizers from two points of view. First he investigated the chemical reactions occurring in such devices, and second he considered the electrical circuit involved. There are, of course, many other researches which we might have chosen for discussion, and again we wish to point out that the choice made is mostly a matter of chance. Since the production of ozone in such an apparatus is of some technical importance (1), it is of interest to know the efficiency of the units employed and to determine the chemical yield per unit of energy consumed. It is necessary then to measure the energy input, and hence the determination of voltage, current and power factor must be studied. A convenient method of applying the voltage to the system is the use of a high-tension transformer. Voltages ranging usually from about 2000 to 25,000 volts are employed. They can be measured by a high-tension voltmeter. The current can be determined by a thermal junction and galvanometer or by observing the voltage drop over a high resistance by means of a quadrant electrometer as is shown in Fig. 24. In this figure T(I) is an autotransformer connected to the alternating current supply which feeds varying voltage to the high-tension transformer T(II) as desired. In the particular arrangement shown the current is measured by determining the drop in voltage over a resistance R_Q by means of an electrometer Q. The resistance R_Q is part of a high resistance $R(ab)$ which should be of the order of 300,000 ohms. The condenser C placed in parallel with the resistance R_Q serves as a by-path for high-frequency harmonics.

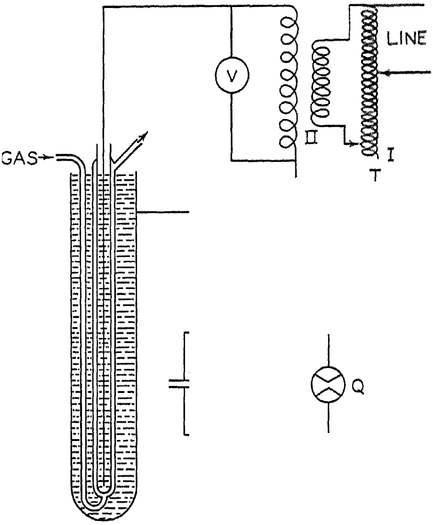

FIG. 24.—Electrical connections for the ozonizer. T = high-tension transformer, V = voltmeter, $R(ab)$ = high resistance (10^3 to 10^5 ohms), R_Q = part of $R(ab)$ across quadrant electrometer, Q = quadrant electrometer, C = condenser (0.1 to 0.2μf), G = ground connection. Warburg, Z. tech. Physik 4, 450 (1923).

Considered as an electrical circuit the ozonizer is seen to be a system of three condensers placed in series. The arrangement of a cylindrical ozonizer is shown in Fig. 25, and the potential variation during the process of charge and discharge is shown after Warburg (8) in Fig. 25. If we consider the electrode d at zero potential and bring a to the potential E then a charge $C \cdot E$ will accumulate on the electrode a if the glass tubes are perfect insulators and C is the total electrical capacity of the condenser system. For further consideration it must be assumed that the next change in the electrical situation, namely, the removal of the potential from *a*, is to take place after any displacement currents in the dielectrics and any ion currents in the gas have vanished. Otherwise the problem becomes unmanageable, especially from the point of view of mathematical treatment. The potential situation brought about by the charging of electrode *a* is shown by curve I of Fig. 25. However, when the potential difference between *b* and *c* becomes large enough an ion current will be set up in the gas space *bc* whereby *c* becomes positively and *b* becomes equally negatively charged. At the same time more charge will accumulate on *a* and the potential in the gas space *bc* will be reduced to a certain minimum value $M(d_2)$ when the ion current in the gas phase will stop and the whole charging process will have come to an end. The potential situation is now shown in curve II, Fig. 25. If the cylinder *a* is now brought to zero potential, the charge $C \cdot E$ would leave it if the gas were non-conducting. The potential assumed by the various surfaces is shown in curve III. The potential difference $V_b - V_c$ is now of opposite sign and larger in absolute value. Hence an ion current will be produced in the gas region until the difference in potential between *b* and *c* has reached the minimum value $M(d_2)$, where further conduction will cease, even though some charges remain on electrodes *b* and *c* and also on plate *a*.

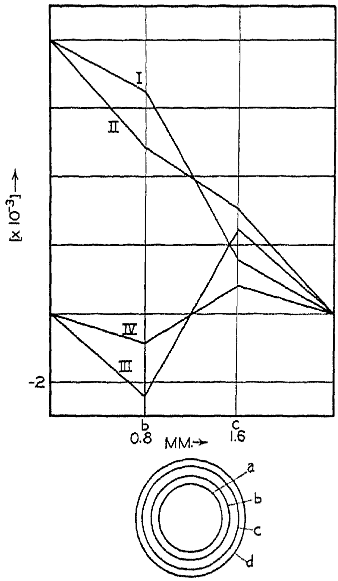

FIG. 25.—(*a*) Potential distribution in an ozonizer during one alternation of charge and discharge. (*b*) Cross-section of ozonizer. V_a = applied potential between *a* and *d*, $V_{bc} = V_b - V_c$, Q = charge on *a*, $\pm q$ = charge on *b* or *c*. C = capacity of condenser, C_2 = capacity of *bc*. Warburg, Verhandl. deut. physik. Ges. 5, 382 (1903).

Mathematical theory of the ozonizer (8). After the ion currents have stopped flowing there will be no free electrical charges located in the interior of the various dielectrics and the situation is then described by

$$\frac{d^2V}{dx^2} = 0 \tag{1}$$

and the potentials are linear functions of the distance. Let

$$-\frac{dV_1}{dx} = \alpha_1 \qquad -\frac{dV_2}{dx} = \alpha_2 \qquad -\frac{dV_3}{dx}$$

or

$$-V_1 = \alpha_1 d_1 \qquad -V_2 = \alpha_2 d_2 \qquad -V_3$$

where V_1, V_2 and V_3 are the potential differences of the condensers $C_1(a-b)$, $C_2(b-c)$ and $C_3(c-d)$. The dielectric constants of glass and gas are ϵ_1 and ϵ_2, and the respective charges on the separate condensers are Q_1, Q_2 and Q_3. Then

$$C_1 = \frac{\epsilon_1}{2ln(r_b/r_a)} \qquad C_2 = \frac{\epsilon_2}{2ln(r_c/r_b)} \qquad C_3 = \frac{\epsilon_1}{2ln(r_d/r_c)}$$

$$Q_1 = C_1V_1 \qquad Q_2 = C_2V_2 \qquad Q_3 = C_3V_3$$

Q_1 = charge on cylinder a
q = charge on cylinder b = $Q_1 - Q_2$
$-q$ = charge on cylinder c = $Q_2 - Q_3$

Then

$$-4\pi Q_1 = \alpha_1\epsilon_1$$

$$4\pi q = -\alpha_3\epsilon_1 + \alpha_2\epsilon_2$$

$$-4\pi q = \alpha_1\epsilon_1 - \alpha_2\epsilon_2 \tag{2}$$

From the last two equations it follows that

$$\alpha_1 = \alpha_3 \tag{3}$$

The potential of a is V_a, and

$$V_a = V_1 + V_2 + V_3 = -\alpha_1 d_1 - \alpha_2 d_2 - \alpha_3 d_3 \tag{4}$$

From (2) and (4)

$$V_a\epsilon_2 + 4\pi q d_2 \tag{5}$$

If C is the capacity of the whole system

$$\frac{1}{C}=\frac{1}{C_1}+\frac{1}{C_2}+\frac{1}{C_3} \tag{6}$$

$$=\frac{V_1}{Q_1}+\frac{V_2}{Q_2}+\frac{V_3}{Q_3}$$

$$=\frac{V_1}{Q_1}+\frac{V_2}{Q_1-q}+\frac{V_3}{Q_1}$$

$$=\frac{(Q_1-q)V_a+qV_2}{(Q_1-q)Q_1}$$

or

$$Q_1=C\left(V_a+\frac{q}{C_2}\right) \tag{7}$$

and since $V_b - V_c = -\alpha_2 d_2$ we find from (2)

$$V_c-V_b=\frac{q-Q_1}{C_2} \tag{8}$$

Warburg defines an apparent capacity for the condenser from (7)

$$Q_1=C\left(V_a+\frac{q}{C_2}\right)=C_S\cdot V_a \tag{9}$$

so that

$$q=\frac{C_S-C}{C}\cdot V_a\cdot C_2 \tag{9a}$$

The total capacity C of the ozonizer can be found by applying such a small potential that no ion current is produced. Then the cylinder a will receive the charge Q° which from (7) is

$$CV_a' \tag{9b}$$

The charges Q° and Q_1 (equation 7) can be determined by means of a galvanometer, whence C and C_S become known since the potentials V_a and V_a° can also be measured and the charge q can be found by means of equation *9a*. The motion of this charge constitutes the ion current which causes the chemical reaction in the gas phase. If the capacities are measured in electrostatic units, the potentials in volts, then

$$q = \frac{C_S - C}{C} \times C_2 \times V_a(\text{volts}) \times \frac{1}{9 \times 10^{11}} \tag{9c}$$

is given in coulombs.

Energy situation in the ozonizer. The energy U of the cylindrical ozonizer is

$$U = \tfrac{1}{2}V_aQ_1 + \tfrac{1}{2}(V_c - V_b)q$$

or using equations 7 and 8

$$U = \frac{1}{2}\frac{Q_1^2}{C} - \frac{Q_1q}{C_2} + \frac{1}{2}\frac{q^2}{C_2} \tag{10}$$

Consider a cyclic process wherein the condenser plate d is kept at zero potential and the cylinder a is brought from zero to some potential V and back again to zero potential. For an infinitely small change in the energy situation, we have

$$dA = dU + dW$$

where dA is the work done on the system, dU is the increase in the energy content and dW is the work expended in the production of the ion current which will appear as heat, radiation and chemical change. Since $dA = V_adQ_1$

$$V_adQ_1 = dU + dW \tag{11}$$

For the whole cycle $dU = 0$ since the ozonizer returns to its initial state and

$$\int V_adQ_1 = W \tag{11a}$$

It has been assumed so far that no free charges exist in the gas which is, of course, not correct when ions are created and move about. If equation 7 is still assumed to apply, then

$$dQ_1 = (C/C_2)dq$$

and

$$(C/C_2)\int V_adq = W$$

These relations will hold after the ion currents have come to rest. The energy calculations indicated can still be made if it is assumed that the ion currents set in after the displacement currents have died out. It does not seem entirely unreasonable to think that this situation meets the actual case.

Minimum potential in gas phase. We have seen that some charges remain on the surfaces a, b and c from former applications of potential to a. Let these values be Q_0, q_0 and $-q_0$, respectively. The potential of a is now zero. If it is changed to V_a then these charges will become $Q_0 + Q'$, $q_0 + q_1$ and $-(q_0 + q_1)$. From equation 7 we see that

$$Q_0 = (C/C_2)q_0$$

$$Q_0 + Q' = C\left(V_a + \frac{q_0 + q_1}{C_2}\right)$$

$$Q_1 = C(V_a + (q_1/C_2))$$

and from equation 8

$$(V_c - V_b)_0 = \frac{q_0 - Q_0}{C_2} = \frac{q_0 - (C/C_2)q_0}{C_2}$$

$$(V_c - V_b)_{V_a} = \frac{-C(V_a + (q_0 + q_1)/C_2) + q_0 + q_1}{C_2}$$

The equations hold after the charging and discharging currents have lapsed. If it is assumed that the two potentials

$$-(V_b - V_c)_0 = (V_b - V_c)_{V_a} = M(d_2)$$

are the same, then

$$q_0 = M(d_2) \cdot \frac{C_2}{1 - C/C_2}$$

$$q_1 = \frac{CV_a - 2M(d_2)C_2}{1 - C/C_2} \tag{13}$$

From these relations it follows that the integral values of the ion conduction currents do not depend on the voltage $(V_b - V_c)_i$ at which conduction commences, but are a function only of the minimum value $(M(d_2))$ at which they cease. From equations 9a and 13

$$\frac{C_S}{C} = \frac{1 - 2M(d_2)/V_a}{1 - C/C_2} \tag{14}$$

or

$$M(d_2) = \tfrac{1}{2}V_a[1 - (1 - C/C_2)(C_S/C)] \tag{14a}$$

From (14) it is seen that the apparent capacity of the ozonizer approaches the value

$$B = \frac{C}{1 - C/C_2}$$

as the voltage V_a increases. This is the capacity of the system when the gas is replaced by a metal ($C_2 \to \infty$). For let

$$C(C_2 = \infty) = B$$

$$\frac{1}{B} = \frac{1}{C_1} + \frac{1}{C_3} = \frac{1}{C} - \frac{1}{C_2}$$

$$= \frac{1}{C}\left\{1 - \frac{C}{C_2}\right\}$$

When the potential of cylinder a is raised to the value V_a a current will be produced in the gas phase if the potential $(V_b - V_c)$ reaches the sufficiently high value found from equation 8:

$$(V_b - V_c)_i = \frac{q_0 - Q_1}{C_2}$$

and from equation 7

$$Q_1 = C\left(V_a + \frac{q_0}{C_2}\right)$$

Substitution and equation 13 give

$$(V_b - V_c)_i = V_a\left(\frac{C}{C_2}\right) - M(d_2) \tag{15}$$

For construction of Fig. 25 the following considerations serve as a guide:

$$V_c = - \alpha_1 d_3 = \left(\frac{C}{C_3}\right)\left(V_a + \frac{q}{C_2}\right)$$

$$V_a - V_b = - \alpha_1 d_1 = \left(\frac{C}{C_1}\right)\left(V_a \frac{q}{+ C_2}\right) \tag{16}$$

where $V_a = V_a$, $q = q_0$, after the displacement current during charging;
$V_a = V_a$, $q = q_0 + q_1$, after the ion current during charging;
$V_a = 0$, $q = q_0 + q_1$, after the displacement current during discharge;
$V_a = 0$, $q = q_0$, after the ion current during discharge.

For a cylindrical ozonizer of the following dimensions: $r_a = 0.76$ cm, $r_b = 0.84$ cm., $r_c = 0.92$ cm. and $r_d = 1.0$ cm. and of a total capacity $C = 0.417 \times 10^{-10}$ farad, Warburg found that the minimum voltage $M(d_2)$ is about 1650 volts and the smallest potential difference which would cause a discharge in this ozonizer is 7000 volts. From these values and the calculated capacity of the gas space bc the lowest difference of potential $(V_b - V_c)_i$ which would produce conductance was found to be 3880 volts. The discharge potential between metal electrodes 1 cm. in diameter and 0.8 mm. apart is 4000 volts.

Current measurements in the ozonizer. We have already indicated (page 35) that the current in an ozonizer can be measured by a thermal junction and galvanometer and by determining the drop over part of a high resistance connected to ground. Warburg (2) has made a careful comparison of these two modes of measurement. He finds that an alternating potential applied to an ozonizer creates higher harmonics (10^5–10^6 per sec.) in the circuit which do not contribute to the ion current and hence do not cause chemical reaction in the present case. Only the fundamental is important in this respect. Of course, this does not mean that high-frequency currents will not produce chemical reaction. Their chemical effect is negligible in comparison to the chemical action produced by the fundamental. The reason may be that the harmonics appear as displacement currents only. The thermal junction will measure the total alternating current (fundamental and harmonics), whereas the quandrant electrometer will measure the 50-cycle current only, especially if a bypass condenser C is included in the circuit as shown in Fig. 24, which permits the higher harmonics to pass around the resistance R_Q. Part of the fundamental will pass the condenser C, and the effective fundamental is given by

$$J = \left(\frac{V_Q}{R}\right)\sqrt{1 + (R_Q C\omega)^2}$$

where ω is the frequency of the alternating-current source. The harmonics (J_h) can be determined by placing a thermal junction in the circuit of the bypass condenser C. Or the total current can be found by connecting the thermal junction at a, Fig. 24. Both methods give checking results. A series of measurements is shown in Table 3.

The yield at zero concentration (A_0) is seen to increase with increase in the gas space of the ozonizer. It is independent of the resistance R because the fundamental current only has been used in the calculations. Furthermore, it does not vary for a tenfold change of frequency of applied potential.

TABLE 3

OZONE FORMATION IN OZONIZER

E. Warburg, Z. tech. Physik. 5, 166 (1924)

Potential E (volts)	Resistance R (ohms) Fig. 24	Current (Fundamental) $J \times 10^6$ (amperes)	$\frac{J_h}{J}$	Ozone Formed m $\frac{\text{Gram}}{\text{Hour}}$	Ozone Concentration in Ozonizer	Yield A_0 grams O Amperes × Hours
50-cycle current; ozonizer gas space: 1 mm.						
8050	313,520	478	2.90	0.245	2.1	518
8130	313,520	561	2.43	0.288	2.5	517
8230	50,000	483	4.57	0.249	2.1	519
8260	10,000	575	8.38	0.291	2.5	510
50-cycle current; ozonizer gas space: 1.54 mm.						
6500	363,520	400	4.43	0.251	2.1	633
6680	100,000	420	......	0.268	2.3	643
6670	10,000	432	6.18	0.269	2.3	628
8450	313,520	619	3.65	0.418	3.4	683
8590	100,000	602	5.05	0.404	3.3	679
9570	313,520	736	......	0.509	4.2	702
9730	100,000	701	......	0.473	3.9	684
50-cycle current; ozonizer gas space: 3.5 mm.						
8980	313,520	435	6.01	0.428	3.5	1003
9060	100,000	442	7.40	0.431	3.6	994
500-cycle current; ozonizer gas space: 1 mm.						
4690	317,520	2542	1.39	1.40	11.0	603
5310	13,000	2893	2.10			
500-cycle current; ozonizer gas space: 1.54 mm.						
4790	317,520	1794	1.66	0.829	6.1	506
5270	13,000	2440	2.96	1.255	8.7	577

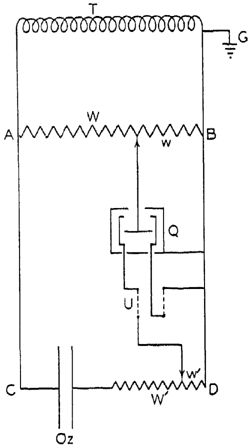

FIG. 26.—Determination of power factor in a circuit containing an ozonizer. T = transformer, G = ground connection, $W(AB)$ = metallic non-inductive resistance of 5×10^5 ohms, Q = quadrant electrometer, U = commutator, Oz = ozonizer in branch CD, W' = precision rheostat of 50,000–100,000 ohms. Warburg and Leithäuser, Ann. Physik 28, 1 (1909).

Power factor in ozonizer circuit. We have seen how the current in an ozonizer can be measured and how therefore the current efficiency (grams ozone per ampere-hour) can be determined. Of further practical importance is the energy yield or the amount of ozone formed per kilowatt-hour. It is necessary to measure the power factor of an ozonizer. Warburg and Leithäuser (9) investigated the power relations, and Warburg (2) has summarized their findings. As has been mentioned, an ozonizer is to be considered as a system of three electrical condensers placed in series. If all the dielectrics involved were perfect insulators then the power factor would be zero and no energy would be consumed in such an electrical system. This would also be true if the gas phase were replaced by a metal conductor. It follows then that for some conductance of the gas phase between zero and infinity the power factor will have a maximum value. If a sine-wave alternating potential (E_0) is applied to the system of perfect insulators described above, then the current is a displacement current and out of phase with the applied potential by $\pi/2$. If the gas phase assumes conductance, then the inner walls of the ozonizer become charged periodically, creating a polarizing counter electromotive force, which will reduce the drop (E_i) over the gas phase and also cause a displacement in phase between E_i and E_a. If the conductance of the gas phase obeys Ohm's law the problem can be solved mathematically. The important quantity is

$$p = \frac{2\pi\Theta}{T}$$

where $\Theta = \epsilon/(4\pi c^2\chi)$ = time of relaxation; ϵ = dielectric constant; c = velocity of light; χ = specific conductivity of dielectric; T = period of the alternating source. For a certain critical value o

$p_c = p_1$ which depends only on the capacities of the compound condenser, the power factor will have a maximum value The arrangement used by Warburg and Leithäuser is shown in Fig. 26. The current in AB is in phase with the applied potential, and the current in $CD(W')$ is in phase with the current passing through the ozonizer *Oz*. The quadrant electrometer served as wattmeter. Its housing was grounded; the quadrants were charged with the drop of potential over the resistance W', which is in phase with the current, and the needle was charged to a potential $V_a(w/W)$ which is in phase with the applied potential. The effective wattage (L) is then

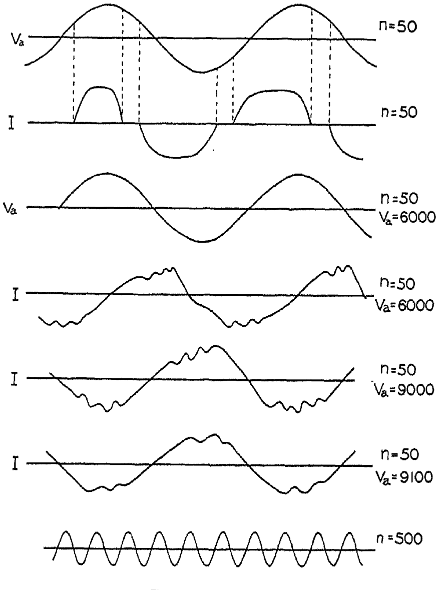

FIG. 27.—Oscillograms of voltage and current in an ozonizer. n = frequency, V = voltage, I = current. Warburg, Z. tech. Physik 6, 625 (1925).

$$L = JV - J^2W'$$

The power factor for various types of systems in the circuit is shown in Table 4. It is unity when the ozonizer is replaced by an ohmic resistance and is less than one when some form of discharge device is replacing the ohmic resistance. Oscillograms of the voltage and current show that they are out of phase, as is seen in Fig. 27.

TABLE 4

Power Factors of Various Appliances at 50 Cycles
E. Warburg and G. Leithäuser, Ann. Physik 28, 1 (1909)

Apparatus in branch *CD* of circuit, Fig. 26	Volts E_a	Current $I_a \times 10^3$	Watts W	Power factor $\cos \phi$
Ohmic resistance (CdI_2 in amyl alcohol, 18×10^6 ohm) in place of ozonizer *Oz*	5,900	3.46	20.5	1.00
Two-point spark gap (luminosity at the point only)	8,500	7.64	61.3	0.94
Point-plate discharge (long positive brush discharge)	9,460	0.548	3.90	0.752
Point-plate discharge (1.5 mm. thick hard rubber plate on the grounded metal plate)	13,280	0.328	1.69	0.388
Metal-ozonizer, with the gas space filled (CdI_2 in xylol and amyl alcohol)	6,900	0.520	2.57	0.716

Energy yield in an ozonizer. Increasing the current density causes a decrease in the power factor, and raising the frequency of the applied voltage produces an increase. A small power factor is undesirable, for only part of the applied voltage is effective in transmitting energy to the ozonizer. A large gas discharge space is advantageous, and metal ozonizers (Fig. 22) are to be preferred. They also pass a much greater current for the same dimensions. Small ozonizers at higher frequencies will furnish as much ozone as larger ones at lower frequencies.

Reaction yields in ozonizer. Warburg (2,10) has summarized several reactions which have been studied in an ozonizer, where electrical measurements were made which permit the calculation of the yields (Table 5). The number of molecules reacting per equivalent of electricity is of the same order of magnitude for the various reactions. It must be said that theoretical considerations pertaining to these reactions, attempting to elucidate a mechanism and to connect kinetic theory impacts with these yields, involve many assumptions and most likely give little insight as yet into the complex phenomena existing in an ozonizer. We have seen, with the reactions in luminous discharge, that no detailed theoretical account can as yet be rendered of the processes occurring in an electrified gas and at higher pressure, i.e., in an ozonizer the situation is no less complicated. However, Warburg (12) has made the attempt to calculate the impacts of charged particles and to relate them to the yields.

TABLE 5

VARIOUS OZONIZER REACTIONS

E. Warburg, Z. Physik **21**, 372 (1924)

Reaction	Gas phase distance d (mm.)	Current density J (amp. per m	Yield Q (moles per coulomb)
	1.54	0.100	3.30
		0.129	4.63
		0.191	9.01
$\frac{3}{2}O_2 \rightarrow O + O_2 \rightarrow O_3$	1.40	0.134	15.50
$2NH_3 \rightarrow N_2 + 3H_2$. .	2.00	0.081	4.23
	2.30	0.084	4.42

Kinetic theory applied to ozonizer reaction. Warburg and Rump (11) have shown that the yield per coulomb of ozone is proportional to the pressure when the oxygen pressure is less than 200 mm. Hg. This situation would indicate that the processes occurring in the ozonizer under these conditions are sufficiently simple to attempt some sort of theoretical treatment. Warburg (12) assumes that the anions are free electrons, which might be so at very low gas pressures. However, we know that oxygen gas has an electron affinity (Chapter XV). In the high field of the ozonizer the electrons will attain considerable velocity during a free path and they will gain speed (u) in the field direction

$$\partial u \tag{1}$$

where γ is the acceleration gained in the field direction. Hence

$$u = \gamma t + u_0 \tag{2}$$

where u_0 is the initial speed at the beginning of the free path. If it is assumed that after an impact all directions of motion of the electron are equally likely then in the opposite case

$$u' = \gamma t' - u_0 \tag{3}$$

and others will lie between the two types cited. If τ is the mean time between impacts and λ is the mean free path, then the mean speed in the two extreme cases is

$$\frac{1}{\tau}\int_0^\tau udt$$

$$\bar{u} = u_0 + \tfrac{1}{2}\,\gamma t^2; \quad \bar{u}' = -\,u_0 + \tfrac{1}{2}\,\gamma t^2; \tag{4}$$

From (2) and (3) we find

$$\tau = -\frac{u_0}{\gamma} + \sqrt{\left(\frac{u_0}{\gamma}\right)^2 + \frac{2\lambda}{\gamma}}$$

$$\tau' = \frac{u_0}{\gamma} + \sqrt{\left(\frac{u_0}{\gamma}\right)^2 + \frac{2\lambda}{\gamma}} \qquad (5)$$

and from (4) and (5)

$$\bar{u} = \tfrac{1}{2}(u_0 + \sqrt{u_0^2 + 2\gamma\lambda})$$

$$\bar{u}' = \tfrac{1}{2}(-u_0 + \sqrt{u_0^2 + 2\gamma\lambda}) \qquad (6)$$

$$\gamma = E\frac{e}{m}$$

where E is the field intensity and e, m are the charge and mass of an electron. If we adopt the mean thermal motion of the molecules (v_a) for u_0 we take a minimum value for this quantity. At 15° C. the thermal motion of oxygen molecules is 43,750 cm. per sec., and the electrons will have a correspondingly higher speed

$$v_a = 43{,}750\sqrt{\frac{m_{O_2}}{m}} = 1.07 \times 10^7 \text{ cm. per sec.} \qquad (7)$$

In order to carry on the calculation a definite case must be chosen. We will consider with Warburg an ozonizer of 0.15 cm. gas space at 50 mm. oxygen pressure:

$$\lambda_{O_2} = 1.52 \times 10^{-4} \text{ cm.}; \quad \lambda_e = \lambda_{O_2} \times 4\sqrt{2} = 8.6 \times 10^{-4} \text{ cm.} \qquad (8)$$

and

$$\gamma_e = E\left(\frac{e}{m}\right) = E \times 1.76 \times 10^7 \text{ e.m.u.} \qquad (9)$$

where E is the radial field strength in the ozonizer and equal to 5.03 $\times 10^{11}$ in the given case, so that

$$\gamma_e = 8.85 \times 10^{18}$$

and

$$(\gamma\lambda)_e = 1.52 \times 10^{16}$$

From (7) we find $u_0^2 = v_a^2 = 1.14 \times 10^{14}$, which can be neglected in respect to $(\gamma\lambda)_e$. Equation 6 can then be written

$$\bar{u} \qquad \overline{\cdot\lambda)}_e = 0.615 \times 10^8 \text{ cm. per sec.}$$

For the cations (O_2^+) Warburg shows that their velocity is only about 0.002 $\bar{u}_e$. The positive ions and electrons will gain the energy $V = E$ while they fall through a mean free path. For the case cited

$$V_e = 5.03 \times 10^{11} \times 8.6 \times 10^{-4} = 4.33 \text{ e.v.}$$

$$V_+ = 5.03 \times 10^{11} \times 1.52 \times 10^{-4} = 0.76 \text{ e.v.}$$

From photochemical experiments we know that the wavelengths 0.207 and 0.253 μ are necessary for the dissociation of the oxygen molecules. These values correspond to 5.96 and 4.88 e.v. It appears that electrons in an ozonizer cannot cause dissociation of oxygen in a single impact but they must traverse distances greater than the mean free path to gain the necessary energy. Furthermore, it is seen that they need to travel considerable distances to gain sufficient energy to ionize the gas. They must surely have opportunity to gain ionization energy, for after all the gas is conducting and the electrons are the most likely agents to produce the ionization needed for the maintenance of the conducting state.

However, we will complete the present analysis of Warburg and consider the current density (J_L) in an ozonizer

$$J_L = 2\pi rl(u_a n_a + u_k n_k)e$$

r = radius of gas space; l = length of gas space; n = number of ions per cubic centimeter; u = velocity; e = elementary charge; a,k = anion or cation. If $u_k \ll u_a$ and $n_k = n_a$ then $n_k u_k \ll n_a u_a$, and

$$J_L \doteq 2\pi rlu_a n_a e$$

the number of impacts per second in the region between r and $r + dr$ is

$$Sdr = 2\pi rdrl\left(\frac{u}{\lambda}\right)n$$

and if the electrons only are considered

$$\frac{Sdr}{J} = dr \cdot \frac{1}{\lambda e}$$

The total number of impacts per coulomb is

$$Z = \frac{1}{\lambda_a \cdot e}\int_{r_b}^{r_a} dr = \frac{d}{\lambda e}$$

and since $e = 1.58 \times 10^{-19}$ coulomb

$$Z = 6.33 \times 10^{18} \frac{d}{\lambda}$$

On the other hand we find the number of oxygen molecules (A_{O_2}) dissociated, from the ozone yield (A)

$$A_{O_2} = \frac{1}{2} A \cdot \frac{1}{48} \cdot \frac{1}{3600} \times 6.06 \times 10^{23} = A \times 1.77 \times 10^{18}$$

and

$$\frac{A_{O_2}}{Z} = \frac{A}{d} \times 0.280$$

For $p = 50$ mm. Hg, the mean free Path is 8.6×10^{-4} cm. and

$$\frac{A_{O_2}}{Z} = 2.41 \times 10^{-4} \frac{A}{d}$$

The results for three different ozonizers are shown in Table 6.

TABLE 6

Oxygen Molecules Dissociated in Ozonizer per Electron Impact

E. Warburg, Z. Physik **32**, 252 (1925)

Gas phase distance d (cm.)	Current yield A gram O_3 per coulomb	$\frac{A}{d}$	$\frac{A_{O_2}}{Z}$
0.10	35	350	0.084
0.15	54	360	0.087
0.35	89	254	0.061

It is seen that 6 to 9% of the electron impacts help towards chemical reaction. The number of electron impacts is inversely proportional to the mean free path and hence varies directly as the pressure. This corresponds to the fact that, at small pressures at least, ozone formation increases with the pressure. Furthermore, these impacts are directly proportional to the gas phase distance (d), and the yield per coulomb does increase with this distance although at a slower rate than proportionality would demand. However, the many assumptions made and the approximate nature of these considerations indicate that the present picture is to be taken as only a first orienting attempt towards an understanding of ozonizer reactions.

Ozone formation with high-frequency currents. Starke (13) studied this question in detail. He used alternating current from 50 to 10,000 cycles per second and determined the energy yield calorimetrically by observing the temperatures of the gas flowing through the ozonizer and the two water cooling systems which constituted the inner and outer electrodes of the ozonizer. It is found that the energy expended in the ozonizer is roughly proportional to the frequency of the applied potential. Variations depend on the change of power factor with frequency. The energy yield (140 grams per kilowatt-hour) and the concentration of ozone (20 grams per cubic meter of oxygen) in the efflux gas do not vary with the frequency. The power factor was determined by comparing the calorimetrically measured energy consumption with the volt-ampere product. This factor increased up to the frequency 3200 and decreased with higher frequencies. As an example it was found in an all-glass ozonizer at 500 cycles to be 0.36; at 4200 cycles, 0.445; and it decreased to 0.37 at 10,000 cycles as Warburg and Leithäuser predicted (page 45). Metal ozonizers are found to be better in the sense that the energy consumed and the power factor are about double the values attained with all-glass tubes. The concentrations of ozone reached are lower. These experiments show that higher frequencies are advantageous for the technical production of ozone since a much smaller number of ozonizers can produce a given amount of ozone and hence first installation costs are considerably reduced.

At high frequencies it is possible to apply a great deal of energy to the ozonizer. Such currents can be produced by oscillating circuits employing the vacuum tubes of radio industry. Since it is likely that further experiments in the electrochemistry of gases will be carried out by such devices, it seems appropriate to describe several circuits in detail. Ozone formation and ammonia synthesis were studied by Wartenberg and Treppenhauer (14) at 23,000 and 300,000 cycles. Their circuit is shown in Fig. 28. The high-frequency currents were produced by a triode of 1.5 kw. The filament was heated by a 17-volt storage battery which furnished 17 amp. The plate voltage of about 3000 volts came from a high-tension generator. A wavemeter controlled the frequency of the output. For 23,000 cycles a blocking condenser C_B (0.09 mf.), consisting of a glass plate oil condenser (5×10^4 cm.) and two Leyden jars of 10^4-cm. capacity each, was used. The primary of a 7-kw. transformer served as a choke coil (D_1). The ammeter A had a paper condenser C_A (0.2 μf.) in parallel to protect it from induced currents. The resonance circuit consisted of a condenser C_1 (two Leyden jars of 10^4-cm. capacity each) and an inductance L_1 made of 1.3-mm. cotton-covered copper wire wound on a wooden frame hexagonal in shape. The coil was 28 cm. in diameter, 17.5 cm. in height. It had 95 turns and a self-induction of 2.1×10^6 cm. Over this coil fitted a secondary of 30-cm. length and 30-cm. diameter, carrying 400 turns of 0.7-mm. cotton-covered copper wire in two layers. The voltage on the ozonizer amounted to 6300–6700 volts, and the current through it was measured by a hot wire milliammeter. For the production of 300,000-cycle current the condenser C_1 was of $1.6\text{-}1.7 \times 10^3$ cm. capacity. L_1 was a coil of 17 turns of copper ribbon (1×10 mm.), 27 cm. long and 34 cm. in diameter, placed on a paraffined wooden frame, having a self-induction of 9.4×10^4 cm. It was placed on a movable stand underneath coil L_2 which hung from the ceiling by an insulator. L_2 was wound on a cylinder 38 cm. in diameter and 60 cm. in length with one layer of 0.7-mm. cotton-covered copper wire. There were 98 turns of copper wire in sections 2 cm. wide at 1-cm. intervals. The best coupling of L_1 and L_2 was found by moving L_1 relative to L_2. L_1 used for 23,000 cycles functioned in place of D_1. The ozonizer constructed as shown in Fig. 28 was made of quartz for the experiments with 300,000 cycles because glass punctured easily. The small bulb placed 1 mm. from the outer wall confined the discharge to a small region of 10- to 15-mm. length; above this section the gas showed very little luminosity. This construction

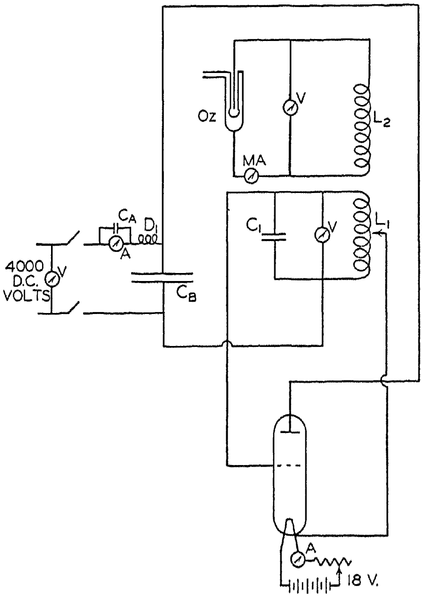

FIG. 28.—Oscillating circuit used for the production of 23,000- and 300,000-cycle current in ozone and ammonia synthesis. v. Wartenberg and Treppenhauer, Z. Elektrochem. 31, 636 (1925).

prevented the breakdown of the ozonizer. The results with this apparatus showed that ozone formation occurs at these high frequencies as it does at lower ones. However, the yields per kilowatt-hour are very low at the rates of gas flow attainable, as also are the concentrations of ozone in grams per cubic meter of efflux gas. The steady-state concentration reached at 500 cycles was about 178 grams per cubic meter; at 23,000 cycles its value decreases to 25 grams per cubic meter, and at 300,000 cycles it only amounted to 1.5 grams per cubic meter. This decrease may be due to the high temperature reached at 300,000 cycles, because then about 170 watts pass per cubic centimeter. By a special experiment Wartenberg and Treppenhauer showed that an ozonizer fed with 300,000-cycle current lowers the ozone concentration of an ozone-rich gas to the same value it itself can produce. In ammonia synthesis it was also found that higher frequencies tended toward lower concentration and energy yield as in the case of ozone formation. They made a rough calculation which shows that the time it takes an electron to gain 10 volts of energy in the field of a given ozonizer is about 10^{-11} sec., while the period of one alternation of a current of 3×10^5 cycles is about 10^{-6} sec. Hence the frequency should have no influence on the chemical action. Any differences found as mentioned above must be due to secondary causes such as increased temperature resulting from insufficient cooling. In other words, with proper arrangements of apparatus high-frequency currents should show the same chemical effect in an ozonizer as low-frequency ones. The reason that Warburg (2) has found only the fundamental of a 50-cycle current to be chemically active, and not the higher harmonics, must then be that these high-frequency currents were displacement currents in the dielectric and did not contribute to the ion current in the gas phase.

Interaction of carbon dioxide and hydrogen. Lunt (15) studied the reduction of carbon dioxide in a quartz ozonizer energized by currents of 1.5×10^7 cycles. The electrical apparatus is shown in Fig. 29. The following are the dimensions of the quartz ozonizer: outer diameter of outer wall, 25.40 mm.; inner diameter of outer wall, 22.15 mm.; thickness of outer wall, 1.63 mm.; outer diameter of inner wall, 15.75 mm.; inner diameter of inner wall, 12.50 mm.; thickness of inner wall, 1.63 mm. The volume of the gas space including capillary-tubing from the entrance to the exit stopcocks was 31.7 cc. The effective length of the electrodes allowing for end effect was 8.75 cm. The dielectric constant of quartz was taken to be 4.0, approximately. The electrical capacity between the surfaces of the reaction vessel was found to be 1.6 $\mu\mu$f per cm. length of reaction space, and the capacity between the electrodes was 1.3 $\mu\mu$f per cm. length. Quartz was chosen for the construction of the ozonizer because glass punctures too easily when used at high voltages and high frequency currents. Lunt also used a coupled circuit where the voltage applied to the ozonizer was due solely to the radio-frequency current. The outer electrode of the ionization vessel was a coat of copper electroplated on quartz and silver plated to prevent tarnishing. The inner tube of the ozonizer was filled with mercury, cooled when necessary by a thin-walled glass vessel carrying water. Pressure changes were determined by means of a mercury manometer. The appearance of the discharge was different from that observed in the ordinary ozonizer. It consisted of a series of

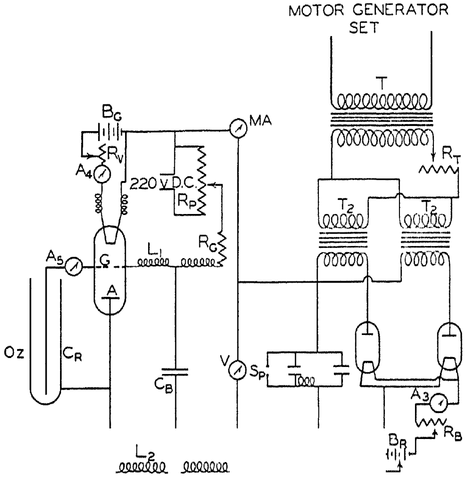

FIG. 29.—Diagram of electrical connections for production of 10^7-cycle current. A = anode of generating valve, A_3 = rectifying valve filament ammeter (0–10 amp. D.C.), A_4 = generating valve filament ammeter (0–15 amp. D.C.), A_5 = high-frequency ammeter (0–10 amp.), B_g = generating valve filament battery (20 volts, 160 A.H.), B_n = rectifying valve filament battery (12 volts, 160 A.H.), C_B = blocking condenser (0.0005 μf.), C_r = capacity of reaction vessel, G = grid of generating valve, L_1 and L_2 = inductances of high-frequency circuits, M_A = generating valve anode current milliammeter (0–200 milliamp. D.C.), O_z = ozonizer, R_B = rectifying valve filament resistance (0–10 ohm, 12 amp.), R_g = generating valve grid resistance (30,000 ohms, 0.01 amp.), R_p = potentiometer resistance (0–6000 ohms, 0.3 amp.), R_t = control resistance of transformer (0–90 ohms, 12 amp.), R_v = generating valve filament resistance (0–10 ohms, 12 amp.), S_p = adjustable safety spark gap set at 7000 volts, T_1 = transformer (3 kv-a., 80/160 volts, 250 ~), T_2 = transformers (1 kv-a., 125/7000 volts, 250 ~) primary windings in parallel, secondary windings in series, V = Kelvin-White voltmeter (0–6000 volts). Lunt, Proc. Roy. Soc. 108, 172 (1925).

sparks and was not smooth and uniform. The maximum voltage that could be applied was about 2000 volts (r.m.s.). It was found that the dielectric strength of a mixture of carbon dioxide and hydrogen reached this value at a pressure of 53 cm. Hg. With a mixture of gases ($CO_2 : H_2 :: 1.023 : 1$) and 150 watts energy being dissipated in the tube, the reaction reached a steady state where carbon monoxide and water were formed as the sole reaction products. The carbon dioxide had decomposed to the extent of about 76% at 50 mm. pressure in 5 min. Increasing the voltage from 720 to 1000 volts and the input from 150 to 500 watts did not affect the proportion of carbon dioxide changed. Hence it appears that the reaction proceeds to a position of equilibrium or a steady state. Lunt calculated an equivalent temperature for the reaction. It is the temperature at which the same relative concentrations would have been reached had the reaction been carried out by thermal means. It ranged from 800 to 1200° K for the conditions of the experiment. In some of the experiments carbon monoxide was reduced mostly to methane, indicating that other changes can take place besides the water-gas reaction. However, no formaldehyde or formic acid were found as reported by Moser and Isgarischew (16). These investigators operated at 50 cycles, and the interesting question arises as to the frequency at which the production of formaldehyde and formic acid ceases. It is also clear that temperature effects as secondary causes must be considered carefully. Lunt (17) has further studied leakage currents in an ozonizer and has described appropriate circuits to measure only the current through it.

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CHAPTER III

CHEMICAL REACTION IN CORONA; ELECTRODELESS DISCHARGE AND ARC

Corona discharge. It is at once seen that the corona discharge observed near highly charged wires is due to the same cause as the discharge near a point. In both cases the electric field near the electrodes of high curvature is high, leading to large forces acting on any free charges present in the gas due to the natural ionization caused by cosmic rays or radioactive contamination. Further ionization by these naturally occurring charges will produce a self-sustained discharge near the wire. The corona occurs near high-tension wires and there constitutes an energy loss. The phenomenon is usually studied in the laboratory by inserting lengthwise a very fine wire (0.01 to 1 mm.) into a large metal cylinder of 5- to 10-cm. diameter. The corona tubes shown in Figs. 30 32 are called semi-corona discharge tubes because the outer cylinder or plate is made of glass with a metal or water electrode on the outside of the glass tubes or plates. The corona is formed near the wire, and the absence of a large metal surface is convenient if chemical investigations are to be undertaken, because any catalytic action of the metal jacket is thereby eliminated. It is clear that the chemical actions obtained in such a semi-corona should be of the same general nature as in the point discharge. The advantage over

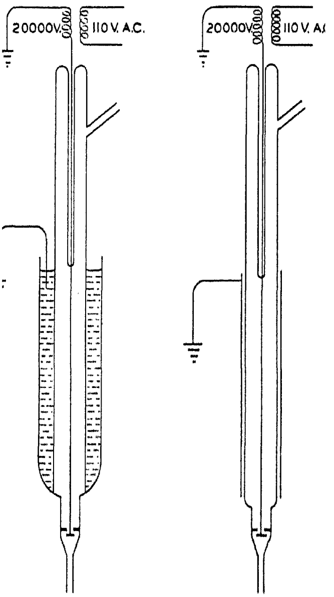

Fig. 30.—Semi-corona ozonizers. Cylindrical type: (*a*) inner electrode is a fine wire and outer electrode is a water-jacket; (*b*) outer electrode is a metal foil.

the ozonizer is the fact that a larger gas volume can be placed under a high electric field. The all-glass ozonizer, on the other hand, is to be preferred when the presence of metal is to be avoided.

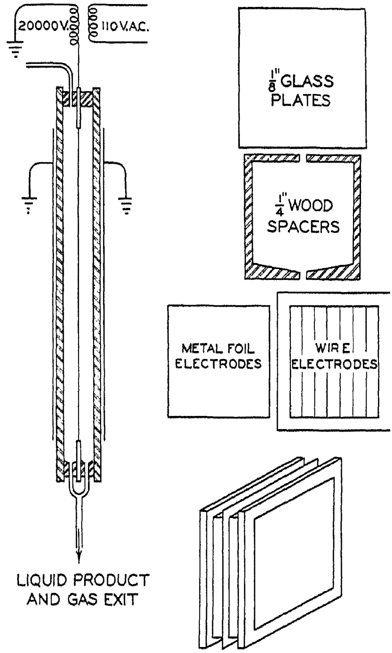
20000V.
110V.A.C.
$\frac{1}{8}$" GLASS PLATES
$\frac{1}{4}$" WOOD SPACERS
METAL FOIL ELECTRODES
WIRE ELECTRODES
LIQUID PRODUCT AND GAS EXIT

FIG. 31.—Semi-corona ozonizer; plate type. Single unit.

The electric intensity E, at the surface of the wire, is given by

$$E = \frac{V}{a \ln(b/a)}$$

where V is the difference of potential between the wire and the surrounding cylinder, a is the radius of the wire and b is the radius of the outer cylinder.

In many cases an empirical law holds

$$E = A + \frac{B}{}$$

where A and B are constants. Variation of the electric intensity with gas pressure can be given by

$$E = E_0 p + c\sqrt{p}$$

when E_0 and c are constants and p is the gas pressure. The two equations can be united into

$$E = E_0 p\left(1 + \frac{D}{\sqrt{ap}}\right)$$

with E_0 and D as constants. The physical and electrical aspects of corona discharges have been treated by Peek (1).

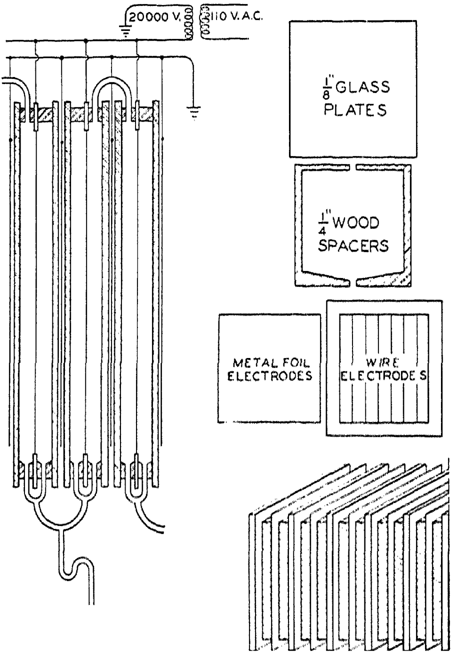
20000 V.
110 V.A.C.
1/8" GLASS PLATES
1/4" WOOD SPACERS
METAL FOIL ELECTRODES
WIRE ELECTRODES

FIG. 32.—Semi-corona ozonizer, plate type. Multiple unit.

Ozone formation in corona discharge. An example of a corona reaction is the work of Warner and Kunz (2). They studied the formation of ozone in an all-metal corona tube. The outer cylinder was about 3.6 cm. in diameter and was made of gold foil 0.15 mm.

thick. The inner wire electrode was a platinum wire about 0.2 mm. in diameter. The corona vessel had a length of 25 cm. Sample results are shown in Fig. 33. The ozone forms near the wire where the high electric intensity causes ionization and excitation phenomena as in the other forms of discharge already discussed.

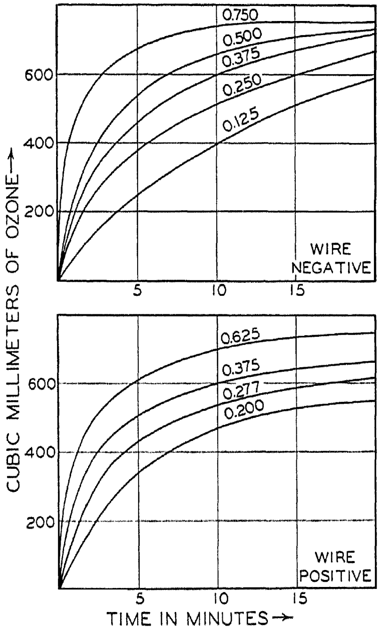

Fig. 33.—Ozone formation in corona discharge for various currents (milliamperes). Warner and Kunz, Univ. of Illinois Bulletin No. 114, Expt. Station (1919).

A comparison of energy yield can be obtained by the use of the following relations:

Amperes × Volts × Power factor = Input; Grams per Coulomb × 3600 = grams per ampere-hour; Grams per ampere-hour × [1000/(Volts × Power factor)] = Grams per kilowatt-hour.

The yields for various discharge types are illustrated in Table 7.

A more detailed study of ozone formation in a wire corona was made by Rideal and Kunz (3), who investigated the distribution of ozone in the neighborhood of the wire. They determined its concentration as a function of the distance from the wire by a chemical and a photo-analytical method. In the chemical method they inserted a fine

TABLE 7

Ozone Yield in Various Forms of Discharge

Type of discharge	A_0 Grams per ampere-hour	B_0 Grams per kilowatt-hour	Reference
Point plate......	500	65	Fig. 23
Glass ozonizer....	600	160	Chapter II (9)
Metal ozonizer...	800	160	Chapter II (9)
Glass ozonizer....	...	140	Page 51
Wire corona.....	...	20	Fig. 33
Wire corona (−).	162	(20)*	Fig. 34
Wire corona (+).	86	(10)*	Fig. 34

* Estimated with power factor 0.5.

glass-capillary into the corona discharge and analyzed the ozone withdrawn, using ordinary chemical means. In the physical method they observed the light absorption of the gas at various distances from the wire. The two methods check satisfactorily, as can be seen from Fig. 34. We see that the negative corona produces higher concen-

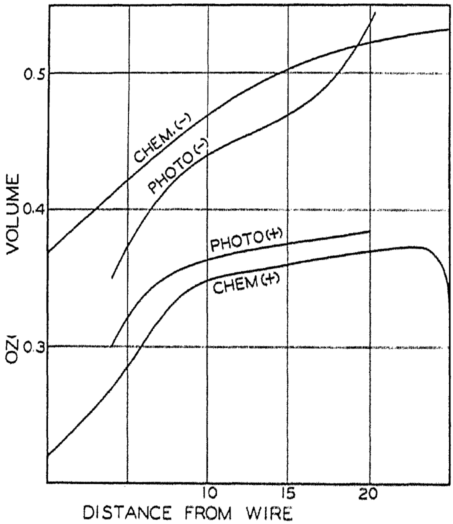

Fig. 34.—Ozone synthesis in wire corona. Wire either positively (+) or negatively (−) charged. Analysis by chemical means or by light absorption. Rideal and Kunz, J. Phys. Chem. **24**, 379 (1920).

trations of ozone than the positive corona, as we might expect from earlier results in glow discharge and in the point-plate discharge. The yields, both per ampere-hour and per kilowatt-hour are smaller. This situation may be due to the fact that ozonization has not been studied in the same detail in the wire corona as it has in the conventional ozonizers of the all-glass and metal types. For we may expect yields in the wire corona of the same order as in the point-plate discharge.

The electrodeless discharge. Another form of discharge which has been used in the study of chemical gas reactions under electrical excitation is the electrodeless discharge. It has the advantage of the ozonizer in the fact that no metal electrodes protrude into the gas phase. A glass tube is placed in a solenoid through which an alternating current of high frequency passes. The discharge is produced by the discharge of a condenser via a spark gap. It appears that two types of field are involved: a field due to electromagnetic induction (I, 2), and an electrostatic one studied by Townsend and Donaldson (4). The electrical equipment used consists of a high-tension transformer, as for example a 1 kv-a. Thordarson transformer giving 25,000 volts on the secondary. A spark gap capable of adjustment with zinc electrodes about 2 cm. in diameter and a 0.02 μf condenser produce a high-frequency discharge. This discharge is sent through a solenoid made of heavy insulated copper wire consisting of a few (perhaps five or six) turns which are wound around the reaction flask. Such an arrangement was used by Harkins and Gans (5), for example, in a study of the chemical effects of electrodeless discharge on certain organic compounds.

Organic compounds in electrodeless discharge. The experimental arrangement used in the study just referred to is shown in Fig. 35. The experiments must be carried out at low pressures (less than 0.1 mm. Hg) because the electrodeless discharge operates best at low pressure. If the pressure should rise during a run, the discharge is extinguished. In the study of benzene vapor several thousand liters of vapor were admitted continuously into the reaction bulb. The benzene was completely converted into a reddish brown solid product. No permanent gases were produced during the reaction. The composition of the solid compound was therefore found to be $(CH)_n$. It was completely insoluble in the ordinary solvents. It had no vapor pressure at 100° C. even when liquid air was used as a condensing medium.

All the unsaturated hydrocarbons form solid brown or black products which are insoluble in water or organic liquids and which doubtless have high molecular weights. Normal heptane, unlike the

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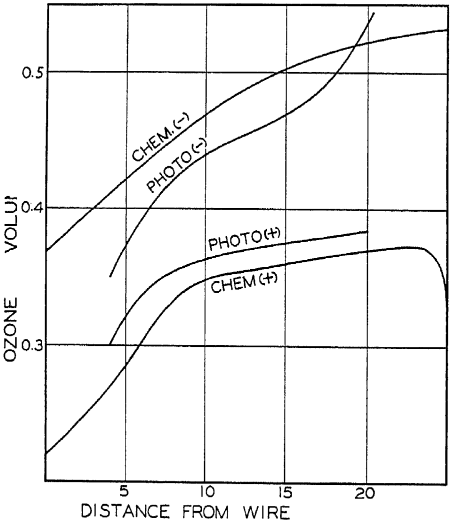

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All the unsaturated hydrocarbons form solid brown or black products which are insoluble in water or organic liquids and which doubtless have high molecular weights. Normal heptane, unlike the unsaturated hydrocarbons, gives only a very small amount of solid product under the experimental conditions in electrodeless discharge. The pressure rose slightly during a run, tending to extinguish the discharge. The emersion of the side tube *E* (Fig. 35) did not remedy matters. No liquid products could be detected.

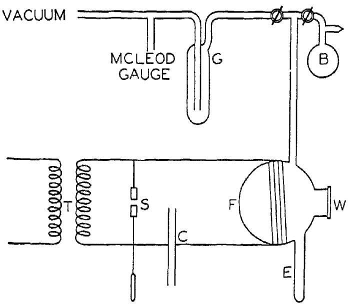

FIG. 35.—Reaction vessel in electrodeless discharge. *T* = transformer, *S* = spark gap, *C* = condenser, *F* = reaction vessel, *E* and *G* = liquid air traps, *W* = quartz window, *B* = supply bulb. Harkins and Gans, J. Am. Chem. Soc. **52**, 5165 (1930).

It is seen that the organic substances mentioned undergo chemical changes in electrodeless discharge as expected. However, the type of product formed is somewhat different from the resulting compounds produced in an ozonizer. The difference must be due to the types of active species formed and to the pressure. The ozonizer reactions are carried out at high pressures where the activated molecules can make many collisions during their lifetime, whereas the pressure in electrodeless discharge must necessarily be low in order that the discharge can continue. In this respect the situation is more like the conditions in the glow discharge, which also operates at low pressures only.

Harkins and Jackson (I, 20) have made a comparison of the actions produced in the electrodeless and glow discharge (Table 8). It appears that the condensation into solid product is more rapid for substances with a small hydrogen-carbon ratio. Benzene, xylene, mesitylene and methane have the H : C ratios 1.0, 1.25, 1.33 and 4.00 respectively, and the rates of formation of solid product in electrodeless discharge are found to be 1.2, 1.0, 0.8 and 0.0 gram per hour.

Harkins and his co-workers (5; I, 20) have also studied the radiation which is emitted from the vapors while in the discharge. The band and line spectra observed indicate the presence of atoms and radicals, and it is necessary to consider these entities as possible reaction centers.

The low-voltage arc. The type of discharge known as the arc is distinguished from other forms by the high temperature in the gas phase and of the electrodes (I, 1, 2, 5). Chemical actions taking place in arcs may then be activated by the electrical processes involved in

TABLE 8

COMPARISON OF REACTIONS IN ELECTRODELESS AND GLOW DISCHARGE

W. D. Harkins and J. M. Jackson, J. Chem. Phys. 1, 37 (1933)

Substance	Color of discharge		Color of product	Form of product	Product (grams per hour)
	Ring	Glow			
(E) Methane....	Green-white	White to red	Light brown	Scales	0.0
(G) Methane....	Blue-green to pink		Black to brown	Powder	0.03
(E) *n*-Heptane...	Blue-white	Reddish white	Yellow brown	Very thin scales	0.00
(G) *n*-Heptane...	Blue-green to pink		Black to brown	Powder	0.15
(E) Benzene.....	Greenish white	White	Medium brown	Powder and small scales	1.2
(G) Benzene.....	Blue-green to white		Black to yellow	Powder and gum	0.5

discharges and by thermal means. Hence the electrochemistry of gases in the arc is not as clear-cut a phenomenon as are the other types of excitation already discussed. There is, of course, some analogy between arc and glow discharge reactions as, for example, the synthesis of ammonia studied by Brewer and Miller (6).

Ammonia synthesis in the low-voltage arc. We have seen (I, 15–18) that ammonia gas can be synthesized in glow discharge from its elements if care is taken to remove the product by immersing the reaction bulb in liquid air, whereby the ammonia gas formed can freeze out on the walls. Brewer and Miller produced ammonia in the low-voltage arc in a similar manner. The arc was maintained between a heated filament and a plate as shown in Fig. 36. The rate of ammonia formation in glow discharge was found to be independent of the pressure over a wide range and proportional to the currents. These findings were expressed in an electrochemical equivalence law (Chapter I). The maximum rate of reaction was found in a mixture $2H_2 : N_2$ and not $3H_2 : N_2$ as might have been supposed. The following questions arise:

Does the proportionality between reaction rate and current also hold for the low-voltage arc? At what percentage of nitrogen will the synthesis proceed with the maximum rate? At what voltage will the reaction set in?

Ammonia formation has been studied by several investigators with electrons of controlled speed (Chapter V), and it has been found that the electrons must have about 17 e.v. of energy before reaction sets in. At certain higher voltages (23, 26, 33, e.v., etc.) increases in reaction rate are observed. The results of the present experiments are indicated in Figs. 37 and 38. It is seen that the rate of formation is independent of the pressure down to very low pressures with a cylindrical plate 1 cm. in diameter and 1 cm. high. At lower pressures the dimensions of the plate exert an influence on the rate, indicating perhaps the complex nature of the phenomena in gases in the sense that any equivalence relations found may be due to the coordination of many factors which give a simple result. The actual proportionality between rate and current is definitely shown in these experiments, however the relation may arise. The reaction sets in at about 16 e.v., as has been found in earlier experiments with controlled electrons. It increases rapidly between 17 and 23 e.v. and is proportional to the applied potential beyond this value. In some cases a clean-up of the gas was found below 17 e.v., but it was shown that water vapor was formed owing to impurities. The oxygen can come from the oxide-covered filament. This had an effect on the synthesis. Longer filaments gave a slower rate. Brewer and Miller think that the longer filaments caused the decomposition of the positive ion clusters and thereby lessened the rate. It is then assumed that positive ions contribute to the reaction mechanism. It is also conceivable that ammonia molecules once formed would decompose on the larger filament before they could reach the cold wall. The arc itself occupied about the same

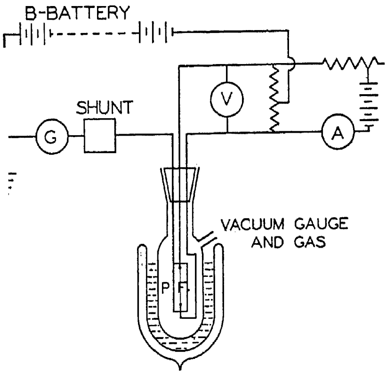

FIG. 36.—Low-voltage arc tube and electrical connections. A = ammeter, V = voltmeter, G = galvanometer, F = filament, P = plate. Brewer and Miller, J. Am. Chem. Soc. 53, 2968 (1931).

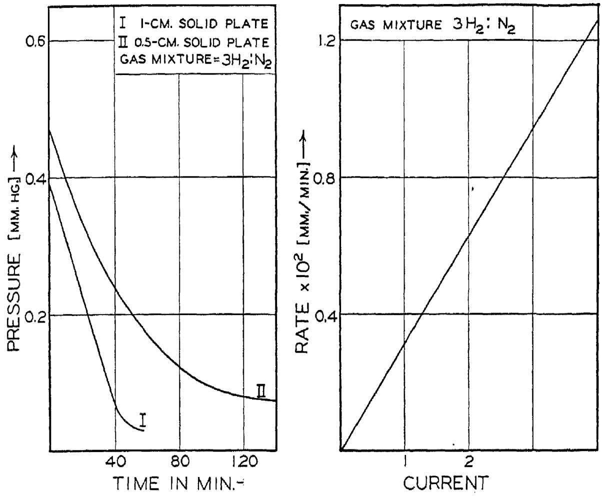

FIG. 37.—Ammonia synthesis in low-voltage arc. Pressure drop as a function of time and reaction rate in dependence of the current. Brewer and Miller, J. Am. Chem. Soc. **53**, 2968 (1931).

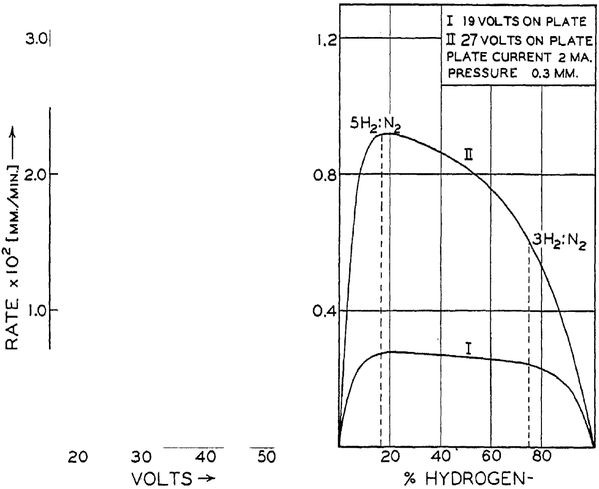

FIG. 38.—Ammonia synthesis in low-voltage arc. Reaction rate as a function of the plate-voltage and gas composition. Brewer and Miller, J. Am. Chem. Soc. **53**, 2968 (1931).

region on the filament irrespective of its length. Excess of nitrogen favors the reaction rate, which reaches a maximum for a gas mixture containing 83% nitrogen. The interpretation given to the processes occurring in the low-voltage arc is the same as that given by Brewer and his co-workers (I, 15–18) for the similar action in glow discharge. The present authors calculate an M/N ratio for the reaction (Table 9). They realize that a computation of the number of ions formed per electron of current involves many uncertainties such as the percentage of the current carried by the electrons, the number of positive ions formed per electron and the distribution of ionization between the nitrogen and hydrogen. The assumption is made that the electrons carry all the current. The relative numbers of hydrogen and nitrogen mole ions is obtainable from the probability of ionization in these gases. The computed results are shown in Table 9. The M/N ratio is practically constant in the range 17 to 20 e.v., indicating a single mechanism, and reaches a high value of 2.25 at 22 e.v. It is difficult to understand on any ion mechanism why the ratio should be greater than 2. The fault may lie with the calculation of the number of ions. The decrease in M/N ratio beyond 22 e.v. is thought to be due to the fact that the mole ions (N_2^+) dissociate into atoms (N) and atomic ions (N^+) upon impact with molecules. If it is assumed that the neutral atom cannot react with hydrogen molecules but that the atom ion can do so, then a decrease in rate can be expected. The mechanism favored by Brewer and Miller is for the N_2^+ ion

TABLE 9

AMMONIA SYNTHESIS IN LOW-VOLTAGE ARC

A. K. Brewer and R. R. Miller, J. Am. Chem. Soc. 53, 2968 (1931)

Volts	Molecules per minute $\times 10^{-17}$	Molecules per electron	N_2^+/e	M/N_2^+
18	0.1366	0.0145	0.0113	1.29
20	0.5766	.0612	.0487	1.26
22	1.730	.1835	.0816	2.25
30	2.885	.306	.1945	1.57
40	4.350	.462	.345	1.34
50	5.770	.613	.487	1.26

$$N_2^+ + 3H_2 \rightarrow (N_2H_6)^+$$

$$(N_2H_6)^+ + E^- \rightarrow 2NH_3(\text{wall or gas phase})$$

and for the N^+ ion

$$N^+ + 2H_2 \rightarrow (NH_4)^+; \quad NH_4^+ + E^- \rightarrow NH_3 + H$$

They admit, however, that the above mechanism is not the only conceivable one in the low-voltage arc.

These experiments show that chemical reactions can be carried out readily in this type of discharge if care is taken to remove the products before they are decomposed by the electrical and thermal agency of the arc.

Sparks and other forms of discharge. We might further illustrate and discuss the reactions in sparks, high-tension arcs, hollow cathode discharges and in luminous discharges with liquid electrodes. However, nothing new or interesting is to be found. It is obvious that chemical reactions will take place in these devices, and that the nature is the same as in those already mentioned.

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CHAPTER IV

CHEMICAL EFFECTS OF CATHODE RAYS

Introduction. It would be a great advantage if it were possible to separate the region where electrons are produced from the reaction space proper, because then any chemical effects due to the hot filament, the glow discharge or the arc could be eliminated in electrochemical gas reactions. This can indeed be accomplished by interposing very thin metal or glass windows which permit the passage of electrons of sufficient velocity but will keep the gas to be studied in the reaction chamber proper. The ions are produced outside of the field, and they do not cause further ionization as they would if they were formed in an electric field. Moreover, the reacting gas can be used under very much higher pressure than otherwise would be possible. The electrons can be obtained in vacuum using a hot filament or a discharge at low pressure. Such tubes, called cathode-ray tubes, are shown in Figs. 39 and 40. Two types have been developed lately, known as the "Coolidge cathode-ray tube" (1) and the "Slack cathode-ray tube" (2). They will be described presently, but it must be mentioned that high-speed cathode rays have been used for many years in the study of chemical reactions.

Coloration of substances. It has long been known that bombardment with high-speed electrons caused the production of color in many substances. For example, halides of the alkali metals are sometimes colored yellow or brown, and sometimes deeper shades, red and blue, are produced. The question immediately arose whether these changes are of a physical or chemical nature. It is also possible to produce such coloration by exposing these halides to the hot vapors of some alkali metal. These studies are still in a controversial state in the sense that it does not seem to be altogether clear even after years of research whether these changes in color do or do not involve definite chemical reactions. Since this topic has been discussed at some length in another place (3) and since the ultimate answer does not seem to have been obtained as yet, it appears unprofitable to discuss this subject in a monograph which is concerned with the electrochemistry of gases.

Cathode-ray tubes without windows. Many early investigations, aimed at a study of the influence of cathode rays, were carried out within single tubes. Both the production of the cathode rays and the study of the reaction were made in the same region. In many cases ionization was produced by impact and no hot filament furnished the electrons. If the substances to be investigated are solids, which can be placed on the anode plate, and if electrons are obtained from a hot cathode by thermionic emission, it is clear that the presence of a window is of no importance, for it is only necessary to maintain good vacuum conditions in the tube. Any gases produced by the impact of the electrons on the anode material must be pumped off efficiently so as not to change the nature of the discharge. Such investigations can be carried out in one tube which serves both purposes: the generation of high-speed cathode rays and the study of chemical reactions they may produce in a solid or liquid of very low vapor pressure.

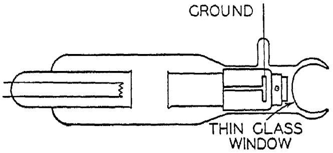


FIG. 39.—Cathode-ray tube with very thin glass window. Slack, J. Optical Soc. Am. **18**, 123 (1929).

A variety of chemical reactions was studied in several investigations (4–7) which were mainly concerned with solid systems. However, in order to show the type of study possible in cathode-ray tubes without a window, the following research is discussed in more detail.

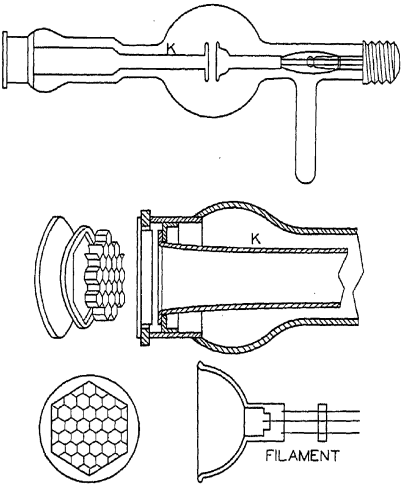


FIG. 40.—Cathode-ray tube with thin metal window. Coolidge, J. Franklin Inst. **202**, 693 (1926).

Rabinowitsch (8) attempted to decompose solid calcium oxide with the idea of relating the minimum voltage of decomposition to the heat of dissociation of oxygen. However, he found that bombardment with 40-volt electrons at best gives a yield of only 0.01%. With the help of sufficiently rapid electrons (cathode rays) of about 1000-volt velocity, decomposition of cerium oxide was shown to take place. Vacuum conditions were very satisfactorily controlled, and a hot filament furnished the electrons. The light yellow cerium oxide (CeO_2) placed on the anode showed after bombardment a dark spot due to the free metal or a lower oxide. Again the efficiency is very low: one atom of oxygen is removed by 400 electrons. A difficulty in these experiments lies in the fact that the substance to be studied must be a conductor at least to some extent or else the anode will charge up negatively to such a high value that no more electrons will reach it and all action will stop. This is a very important consideration and makes it difficult to study non-conducting materials.

The development of the modern cathode-ray tube will now be traced. It will be seen that the voltage and therefore the speed of the electrons, the power, the current and hence the number of electrons have been increased tremendously since the earliest work of Lenard.

Lenard rays. Lenard (9) was the first to replace the usual anode of a discharge tube by a thin window which permitted the electrons to leave the generating tube or the discharge region where they were produced. It was then possible to study the effects of cathode rays or electrons alone. Lenard states that P. Hertz (10) discovered the fact that cathode rays can penetrate thin foils of metals such as gold, aluminum and others, and Hertz suggested to him the use of thin metal foils as windows for cathode-ray tubes. Lenard made an aluminum window 0.0026 mm. thick and fastened it by means of marine glue over the 1.7-mm. opening of a brass cap. The brass cap was the anode of a discharge tube. The tube was operated from an induction coil, and the voltage used corresponded to a 3-cm. spark between small metal spheres. The air in front of the tube showed luminescence for a distance of 5 cm., and fluorescent substances such as lime and others gave luminous effects for even greater distances from the window, i.e., 6–8 cm. Lenard found that ozone is formed near the window and that the cathode rays have an effect on the photographic plate as had been shown by Goldstein (11). A mixture of hydrogen and oxygen (electrolytic gas) when blown against the window did not explode, nor did hydrogen sulphide placed in a tube fastened to the window show any signs of decomposition in the sense that a sulphur deposit could be noticed. Nor did a stoichiometric mixture of hydrogen and nitrogen when placed under the influence of the cathode rays show any ammonia formation. Some of these cases have been studied since, and it will be seen that such chemical reactions are indeed possible. Lenard noticed a volume increase with all gases which is due to a heating effect caused by the cathode rays. The kinetic energy of the electrons after leaving the window and upon absorption in the gas will cause a rise in its temperature and therefore a slight increase in the volume. He (12) studied the absorption of cathode rays in various materials and found that their absorption is mainly a mass effect in the sense that the kind of matter involved is only of secondary importance whereas the density of the absorbing layer is of primary significance. For a 10^7-fold variation in density he noted that the absorption power and density are related as follows:

$$\frac{\text{Absorption power}}{\text{Density}} = \frac{\alpha}{D} = 3200 \frac{\text{cm.}^2}{\text{gm.}}$$

where D = density in grams per cubic centimeter and α = the reciprocal of the distance which will reduce the cathode-ray beam to the "one over *e*th" part of the initial intensity. Hydrogen is an exception. Lenard (13) has studied the physics of cathode rays extensively for many years, and much information has been obtained as to the absorption of these rays of varying speed, their energy losses while traversing material bodies, the production of secondary rays, X-rays and light when they impinge upon matter.

Attempts were made immediately to improve the design of the original Lenard tube, and Des Coudres (14) made a small cathode-ray tube of hard rubber, operated by a Tesla coil and fitted with an aluminum window 0.003 mm. thick. The window end of the tube was grounded as Lenard had done before him. He showed that weak X-rays are produced in the aluminum window and that the air near by is conducting because an electroscope can be discharged by it.

The two tubes described above had one window of small diameter which could withstand atmospheric pressure on one side. Pauli (15) improved this design by supporting a large aluminum sheet by a brass cap covered with copper gauze. The brass cap was perforated with 20 holes, 2 mm. in diameter and closely spaced. The copper gauze was made of wire 0.1 mm. in diameter, and the wires were 0.23 mm. apart. It was necessary to grind the gauze smooth on the side towards the aluminum foil so that the foil would not tear. This window withstood 50,000 discharges and gave more intense rays than could be obtained from a thicker or an unsupported window. Pauli had also tried other windows: oiled silk paper, tissue paper, various kinds of silk, cambric, thin quartz and glass windows, but found none of these materials satisfactory, for various reasons. The quartz and glass films were quite transparent when thin enough, but only very small pieces could be obtained of uniform thickness. These tubes were made for demonstration purposes, and the usual fluorescence and absorption phenomena of cathode rays could be shown to a large audience.

Another ingenious modification of the original Lenard-tube is due to Pauli (16). He made the window of two platinum diaphragms (0.05-mm. thickness), each pierced with a small hole (0.01-mm. diameter) and used powerful pumps to remove gases from the region between the two diaphragms. The cathode rays can leave the generating tube through the small holes and enter the atmosphere of the room or any other gas placed in an appropriate container in front of this "window."

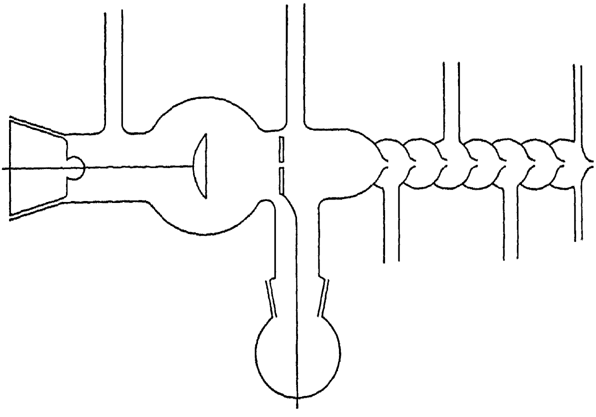


Fig. 41.—Cathode-ray tube. Peters and Schlumbohm, Naturwissenschaften 14, 718 (1926).

With the development of thermionics it was a foregone conclusion that the gaseous discharge used to produce electrons by impact ionization would be replaced by a hot filament in a very good vacuum. Eisenhut (17) appears to have been the first one to make this important change, and Krüger and Utesch (18) described a similar tube which they used in a study of ozone formation to be discussed below. They used a transformer for the production of the high potential and rectified by means of a kenotron.

Peters and Schlumbohm (19) built a cathode-ray tube (Fig. 41) following the principle of Pauli but increasing the number of orifices. They placed seven chambers at the anode end, each carrying an orifice 1 mm. in diameter. These holes were all lined up and the chambers were evacuated by twelve powerful pumps. With this arrangement they were able to reduce the pressure in the seventh chamber, where the hot-wire cathode was located, to about 0.002 mm. The large number of pumps required make this apparatus excessively expensive. While the use of a metal window is of course avoided by this method of construction it remains to be seen whether large streams of electrons can be liberated into the atmosphere through such a set of orifices.

The Coolidge cathode-ray tube. The cathode-ray devices described so far have been useful only at rather low voltages and currents when compared with the modern X-ray tubes. Coolidge (1) therefore took up the further study and development of the production of high-voltage cathode rays outside the generating tube. These modern devices can be used at voltages up to 350,000 volts and operate at several milliamperes. They emit through their windows the most intense stream of electrons so far produced. They can be sealed off from the evacuating system. One type of tube useful for voltages up to 250,000 volts is shown in Fig. 40. Since the Coolidge tube has been used in most of the chemical investigations recorded below, it is necessary to describe it in some detail.

The cathode. The size and shape of the cathode are of importance because they determine the area of the window hit by electrons, i.e., the focal spot. The electrons should impinge on the window as evenly as possible so as to avoid local overheating. The filament is made of tungsten wire 0.0216 mm. in diameter, coiled into a flat spiral 0.5 cm. in diameter and mounted in a focusing cap 2.5 cm. in diameter made of molybdenum. The filament and its mounting are shown in Fig. 40.

The anode shield. This thin copper tube (*K* in Fig. 40) serves to protect the glass from being punctured near the anode and is very important for high-voltage operation. No electron can reach the glass wall, and very few of the initial stream from the cathode impinge on the interior wall of the shield, because it is so designed that all the electrons go to the window. Of course, electrons reflected from the window and secondaries therefrom reach the shield. The end of the shielding tube towards the cathode is rounded to prevent cold discharges.

The window. From Lenard's study of the relation of absorption of cathode rays and density of material it is obvious that a window should be made of as light material as possible. For this reason aluminum foil had been used by most investigators. However, other factors are of importance, and Coolidge made a very careful study of this problem. He considered ductility, resistance to oxidation, heat conductivity, elastic limit and possibility of soldering and brazing the material to the frame, and he finally produced nickel windows free from holes consisting of sheets 0.0127 mm. thick and 7.5 cm. in diameter. Such windows could be fastened to the inner frame by means of soft solder.

The window support. A honeycomb structure made of molybdenum served as a supporting grid for the window; it is shown in Fig. 40. Only 20% of the total area of the window is covered by the grid.

High-voltage sources. The earlier cathode-ray tubes had been activated by induction or Tesla coils, and only in a few had high-voltage transformers been used to produce the potential needed to drive the electrons from the cathode through the thin anode. The high-potential source used to operate the cathode-ray tube is of course of great importance, and Coolidge studied various means for producing them. He used seven different arrangements: (1) an induction coil driven by a mercury turbine interrupter; (2) an induction coil with a Wehnelt electrolytic interruptor; (3) a 60-cycle high-voltage transformer; (4) transformer with direct current superposed on alternating-current excitation; (5) transformer with Tungar rectifier load in the primary; (6) transformer with mechanical rectifier; (7) constant-potential continuous current produced by a 2000-cycle transformer-kenotron-condenser outfit.

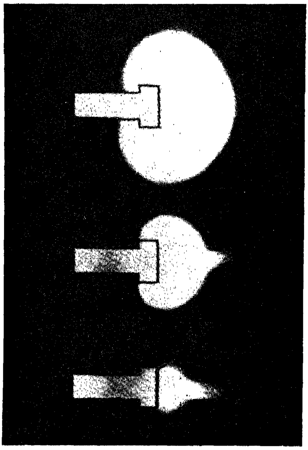


FIG. 42.—Record of cathode rays obtained by direct action of the rays on photographic films. Coolidge, J. Franklin Inst. 202, 693 (1926).

Protection of the operator. It is important to remember that not only will the anode region of such a tube emit cathode rays but that also X-rays are produced in the window and in all objects that come within the cathode-ray beam. The persons operating such a high-voltage tube must be properly protected from these various rays. Also it is customary to ground the anode end of the tube.

Cathode-ray intensity. The intensity of the cathode rays outside of the window can be controlled by adjusting the filament temperature. Screens and perforated sheets of metal are not satisfactory.

The distribution of the cathode rays in front of the window is shown in Figs. 42 and 43. It may be studied by the luminosity of the air, by the direct photographic action of the rays and by the range measurement with lime. A position in front of the window can easily be found where a piece of lime shows its characteristic *orange* luminescence. A very faint luminescence at greater distances is due to X-rays. The effect of window thickness on the range of 200,000-volt cathode rays is shown in Fig. 44. By extrapolation it is seen that their range in nickel is 0.081 mm. and in air (zero window thickness) 46.6 mm. For higher voltages Coolidge suggests using the cathode ray tubes in cascade as shown in Fig. 45.

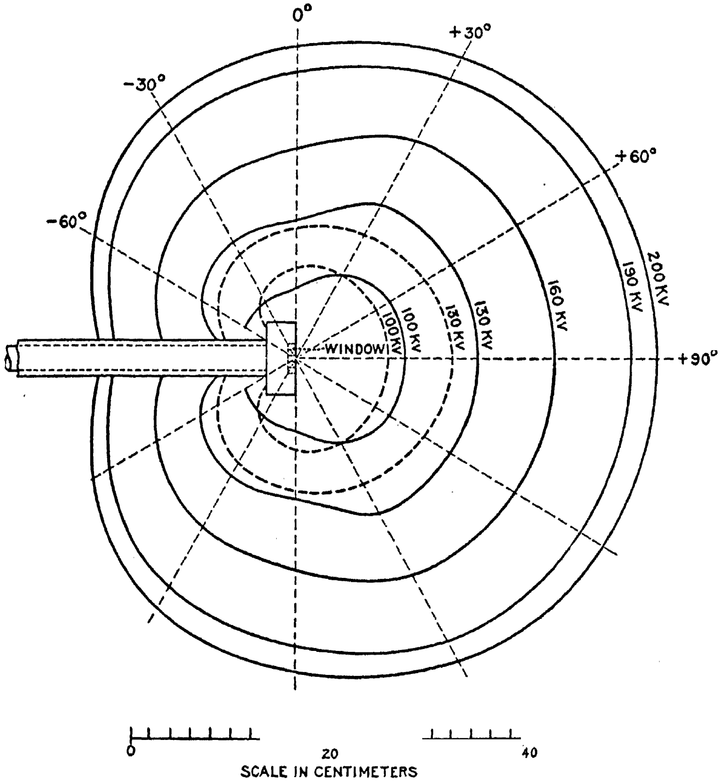

0°
+30°
-30°
+60°
-60°
+90°
200 KV
190 KV
160 KV
130 KV
130 KV
100 KV
100 KV
WINDOW
0
20
40
SCALE IN CENTIMETERS

FIG. 43.—Diagram showing range of cathode rays, as obtained by means of lime and by direct action on photographic film. Window of aluminum 0.0254 mm. thick. Coolidge, J. Franklin Inst. **202**, 693 (1926).

With such a cathode-ray tube Coolidge and Moore (20) carried out studies on the raying of diamonds, fused quartz, halite, calcite and insulators, which effects are physical in nature and are of no particular interest here. The following chemical effects were studied.

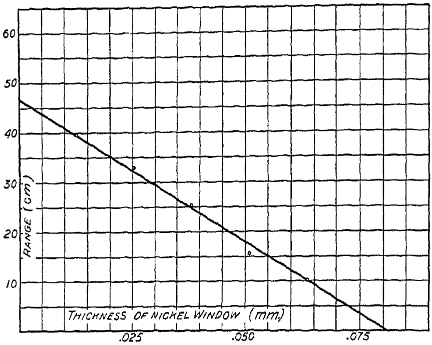


FIG. 44.—Graph showing effect of window thickness on range in air of 200,000-volt cathode rays. Coolidge, J. Franklin Inst. **202**, 693 (1926).

A sheet of glue was exposed to cathode rays in two spots, and, after heating, gas bubbles appear showing that the material has been disintegrated by the rays as can be seen from Fig. 46. Similar action was

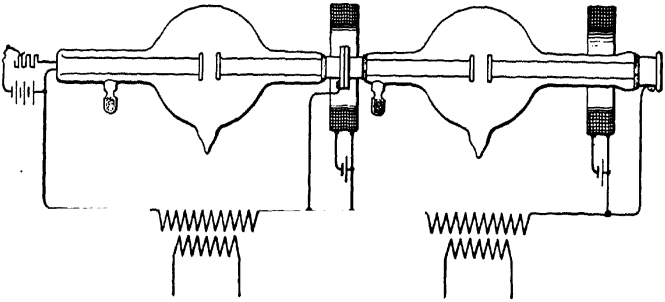


FIG. 45.—Diagram of cathode-ray tubes mounted in cascade for very high voltage. Coolidge, J. Franklin Inst. **206**, 693 (1926).

noted with gelatin, shellac, cane sugar, Rochelle salt crystals and celluloid. Exposure to cathode rays produced acidity in aqueous solutions of cane sugar, starch and glycerine. Milk and butter become rancid;

bacteria can be killed by exposure to the electron stream, as can be fruitflies, snails and cockroaches; plant tissue dries up, and animal tissue is destroyed. Much work has been done in the medical field with beta rays, but now it is possible to extend such research because we can control the energies of these rays by the use of the modern Coolidge tube.

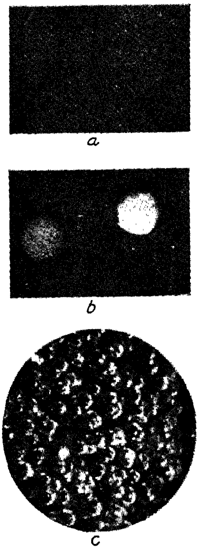


Fig. 46.—Glue exposed over two small areas to cathode rays and subsequently heated: (*a*) after exposure and before heating; (*b*) after heating; (*c*) portion of the one of the exposed areas of *b*(× 100). Coolidge and Moore, J. Franklin Inst. **202**, 730 (1926).

Slack Lenard tube with glass windows. Slack (2) has overcome the difficulty in making glass windows sufficiently thin to permit electrons to traverse them and at the same time of sufficient strength to withstand atmospheric pressure. The windows are blown in the shape of a very thin bubble. For example, a window 2.5 cm. in diameter and as thin as 0.0005 cm. will stand atmospheric pressure when applied so as to put a tension strain on the glass. Such tubes can be baked out at 500° C. without any noticeable weakening of the window (Fig. 39).

The energy loss in any window as given by Terrill (21) is

$$V_0^2 - V_x^2 = K \times \rho \times x$$

where V_0 = the initial voltage through which the electrons have fallen; V_x = the energy the electrons have after traversing the thickness x of the material of the window, expressed in equivalent volts; K = a constant; ρ = the density of material of the window; x = thickness of the window. It is seen that the energy loss is a function of the density of the window material and the window thickness, and it is desirable to keep these two quantities as small as possible. The density of glass is about the same as the density of aluminum, and hence there is no disadvantage in the use of glass windows. A great advantage lies in the fact that no brazing or soldering or cementing is necessary to fasten the window proper to the tube.

No supporting grid is needed for the glass window, and so any loss on this account is avoided. The question arises as to the accumulation of negative charges on the non-conducting glass window. This difficulty was overcome by putting a conducting coat on the window from the anode lead-in to a point beyond where the rays emerge from the window.

Such an all-glass cathode-ray tube has been used successfully in a chemical investigation concerning the condensation of gaseous paraffin hydrocarbons by Lenard rays (50).

The highest velocity cathode rays brought into the atmosphere through an aluminum window were produced by Vollrath (22), who modified the high-potential X-ray tube of Lauritsen and Cassen (23) by adding a Lenard window of aluminum. He obtained 35 microamp. of electrons through the window with a velocity of 600,000 volts and studied the velocity spectrum of these rays, but so far no chemical studies are reported. It is interesting to note that these rays have 90% the velocity of light.

Cathode-ray reactions. The high-speed cathode-ray tubes described in the foregoing section have been used for producing electrons of 80,000- to 120,000-volt velocity, and a variety of chemical changes have been studied with them. Since the primary effect of the high-speed electrons is to produce ions in the gas, it is obvious that such chemical reactions activated by fast electrons must be very similar in character to radon-activated reactions. In the latter case the alpha particles produce ionization, and beyond this point the reaction mechanism may well be the same in both types. Alpha-ray reactions are studied and classified by determining the ratio M/N or molecules reacting or formed per ion pair. The same interpretation may well be adopted for cathode-ray reactions. In either case the course of the change must be followed by determining the number of molecules reacted or formed. In alpha transformations the total number of ion pairs can be calculated readily. However, in the case of cathode rays the procedure is as follows (24): It is known that the energy (E) needed to produce an ion pair (N) in air is $E/N = 32.2$ e.v. (25). In other gases this work will be smaller the greater the relative ionization in the gas as compared to air. It may further be assumed that the total ionization of a gas relative to air is the same for a stream of alpha particles as for one of electrons. It is then possible to find out the energy necessary to produce an ion pair in any gas.

The electrons leaving the window can be caught in a calorimeter (26) and their energy measured. The energy (E) expended for the reaction of one molecule can be found and expressed in volts per molecule giving the ratio E/M. The comparison of these two ratios yields M/N.

Cathode-ray reactions studied in the way indicated are shown to be indeed comparable to radon reactions, and, since it is much easier to obtain equipment for the production of fast electrons than it is to obtain enough radium, many studies will no doubt be carried out with cathode-ray tubes rather than with alpha rays.

Ozone formation by cathode rays. Lenard noticed that the air in front of the window of his cathode-ray tube became ozonized, and Krüger and Moeller (27) used a tube made of ebonite as designed by Des Coudres (14) in a study of ozone formation from oxygen. The ozone was determined by observing the absorption spectrum of the gas after exposure to the electron stream. At the same time they also measured the ionization produced in oxygen by the saturation current method. The amount of ozone formed was found to be much greater than the ionization in oxygen assuming that one ion pair would produce two ozone molecules. When, however, the ionization was measured under the same conditions in nitrogen, it was found that the number of ozone molecules formed per unit time in oxygen is of the same order as the number of ions produced in the inert nitrogen. This seems to point to a disturbing effect on the part of a chemical reaction on the measurement of ionization produced in a gas. However, no great reliance can be placed on these results as many of the quantities involved were very difficult to measure with the equipment available at the time these experiments were carried out. The problem was then attacked anew with a greatly improved cathode-ray tube. Krüger and Utesch (18) carried out this investigation with great care. They used a flow system to avoid deozonization and obtained enough ozone in any one experiment to determine its quantity by the usual chemical titration of iodimetry. The number of ion pairs formed in the oxygen gas before the window was determined by measuring the saturation current in the usual manner. It was shown that the number of ozone molecules formed per ion pair is 20–40 and that there are more ozone molecules formed for the larger currents. The former findings of Krüger and Moeller (27) that ozone formation is equivalent to ionization in an inert gas (N_2) could not be verified. McLennan (28) had shown that the secondary emission in oxygen, nitrogen, hydrogen and air is proportional to the density of these gases, as is to be expected. It appears then that the reaction does not depend on ionization primarily but that excited states of oxygen molecules can produce a reaction mechanism leading to the formation of ozone. This is to be expected when it is recalled that photochemical ozone formation is possible at light frequencies which are not able to ionize the oxygen molecule.

The efficiency of ozone production (gram ozone formed per ampere-hour) for cathode rays was studied as a function of gas flow, voltage and current; for the particular window used, 150 grams of ozone were formed per ampere-hour. This efficiency is much smaller than for an ozonizer (page 60), but it must be considered that the energy of the cathode rays which managed to get through the window is only about 4% of the total electrical energy applied to the tube.

The energy balance for ozone formation is found to be as follows: about 3% of the total energy applied to the cathode rays is used in producing ionization, roughly 8% for ozone formation and the remainder or about 89% for heating the gas. The large number of ozone molecules calculated as formed per ion pair is surprising when the corresponding alpha ray reaction is recalled with $M/N = 2$. The ionization measured by saturation current must be too low, probably on account of inefficiency of the condenser used to catch the ions.

Ozonization was again studied by Marshall (29), who used a Coolidge cathode-ray tube which could be operated continuously at 0.001 amp. and 200,000 volts. It was shown that the reaction occurs entirely in the gas phase and that it is uninfluenced by the walls of the vessel. Fifty per cent of the change occurs within a few centimeters of the window. Ozone is both formed and decomposed by a cathode-ray beam. A steady state is reached upon continued exposure to cathode rays with one molecule of ozone per 1700 oxygen molecules, which is much less than is obtained in an ozonizer where the steady-state concentration is one ozone molecule in twelve of oxygen. It appears then that high-speed cathode rays have a very great decomposing power for ozone molecules. Marshall also tried to measure the ionization produced in the gas by determining the saturation current, but he was not able to attain saturation as apparently Krüger and Utesch had been able to do. It was therefore impossible to check their values (20 to 40) for the numbers of molecules of oxygen reacting per ion pair formed.

However, Busse and Daniels (26) studied the same reaction and were able to make an interesting advance. Using a Coolidge tube they found ozone formed and decomposed. They measured the energy of the cathode rays by a very ingenious method. The high-speed electrons were allowed to impinge upon a calorimeter instead of the reacting gas. The energy they expended in the gas could so be determined. In this manner they found that 8.6 cal. of energy were expended by the cathode rays in oxygen and that at the same time 25 micromoles (1.5×10^{19} molecules) of ozone were obtained. Taking the ionization potential of oxygen to be 15.0 e.v., no more than 1.5×10^{19} pairs of ions can be produced by the above energy. In other words, about one ozone molecule is formed per ion pair, which checks Lind's result (I, 7) but is not in agreement with Krüger and Utesch who obtained $M/N = 20$ to 40.

It is clear from these experiments that ozone can be obtained by high-speed electrons but that the deozonizing effect is more pronounced here than in an ozonizer. The efficiency of ozone formation deserves further study.

Nitric oxide decomposition. This gas is decomposed into nitrogen and oxygen when cathode rays impinge on it. The resulting oxygen will combine with the nitric oxide, producing nitrogen peroxide. Busse and Daniels (26), who studied this decomposition, found that 200 molecules of nitric oxide were removed per electron crossing the tube.

Decomposition of nitrous oxide. Gedye (30) investigated this decomposition by means of fast electrons and found that

$$4N_2O \rightarrow 3N_2 + 2NO + O_2; \quad 2NO + O_2 \rightarrow 2NO_2$$

Each molecule decomposed requires 8.1 e.v. of energy for its destruction, which on the assumption that 31.6 e.v. are needed for ion formation gives $M/N = 3.9$, which checks the alpha-ray reaction.

Carbon dioxide. It is most interesting to note that Busse and Daniels (26) found the action of cathode rays to be such that the results of their experiments were quite unsatisfactory. These experiments were difficult to reproduce, carbon monoxide and ozone being obtained, however. Only three molecules of carbon monoxide were produced per electron crossing the tube. This decomposition is very slight and checks the results of Lind (I, 7), who found that alpha particles do not effect any change in the gas. This situation brings out the relation that exists between cathode-ray reaction and alpha-particle activation. In both cases the ionization produced is responsible for further action, and one may well expect an analogy in the general reaction scheme produced by these two modes of activation as is shown in this case by lack of reaction.

Carbon monoxide. Electric discharge (31, 32) and alpha-ray activation (33) cause the production of carbon dioxide and a suboxide of carbon. Fast electrons give the expected reaction, and McLennan and Glass (34) report that the pressure decrease is due to the formation of a brown deposit on the walls of the reaction vessel and carbon dioxide is formed:

$$5CO \rightarrow 2CO_2 + (C_3O)\text{ solid}$$

Oxidation of carbon monoxide leads to carbon dioxide, and strangely water vapor has an inhibitory effect on this oxidation.

Hydrogen-oxygen combination. It was to be expected that the two gases hydrogen and oxygen would react under the influence of cathode rays and the products might be water, hydrogen peroxide and ozone. All were found by Marshall (35) to be primary products of the interaction of hydrogen and oxygen activated by high-speed electrons (180,000 volts, 0.8 milliamp.). The production of hydrogen peroxide is almost independent of the varying concentration of hydrogen and oxygen, whereas water vapor and ozone formation parallel one another closely at all concentrations, showing that the same primary mechanism is responsible for both. The gross rate of reaction agrees with the rate found by Lind (I, 7). This shows again the close relation which must exist between the cathode-ray- and alpha-particle-activated reactions.

Ammonia decomposition. Lenard (9) had attempted in his earliest experiments to synthesize ammonia gas from the elements and had no success. McLennan and Greenwood (36) studied the reverse reaction, namely, the decomposition of ammonia gas under the influence of cathode rays. They used a Coolidge-type tube which carried on the window side a reaction vessel which could be evacuated or filled with gas as desired. The progress of the decomposition was indicated by the pressure changes within the reaction vessel. A doubling in pressure would indicate complete decomposition of the ammonia.

Wall reaction was avoided by using aged vessels, and decomposition due to silent electric discharge was obviated by proper shielding. It was then found that no ammonia gas was decomposed unless the voltage applied to the tube was greater than 82,000 volts. This voltage is required to force the electrons through the metal window of the tube. For higher voltages the percentage of gas decomposed is proportional to the applied voltage. No decomposition could be observed above 4 mm. of pressure of ammonia, and below 0.68 mm. the decomposition became very rapid. The rate of decomposition (dp/dt, millimeters per minute) is independent of the ammonia pressure for constant voltage and current. This means that each electron decomposes a definite number of ammonia molecules. The rate of decomposition increases with the electron speed. Excess nitrogen augments the quantity of ammonia decomposed, and excess hydrogen decreases the amount of decomposition. Evidently the law of mass action, as ordinarily applied to chemical systems, is not valid for these experiments. Excess nitrogen has no effect on the speed of decomposition, but hydrogen lowers it.

Since a steady state has been reached in these experiments it must mean that ammonia synthesis should also be possible by means of cathode rays. It is rather remarkable that the steady state should be almost entirely on the side of ammonia formation, whereas with most forms of activation the uncombined gases hydrogen and nitrogen predominate in the equilibrium mixture. Gedye and Allibone (24) did not confirm this equilibrium when they studied ammonia decomposition by means of cathode rays. They found hydrazine among the products of decomposition. The relative yield of hydrazine was greater at lower pressures. They measured the energy of the electrons entering into the reaction vessel by means of a calorimeter, and they found 1.2 molecules of ammonia decomposed per ion pair, which result compares well with the ($M/N = 0.8$) ratio obtained by Wourtzel (37) for alpha-ray reaction.

In determining the number of ion pairs produced by the electrons in the reacting gas, Gedye and Allibone use the value 32.5 ± 0.5 e.v. per ion pair obtained for air by Eisl (25). They assume that the total ionization in a gas relative to air is the same for alpha particles and electrons. For example, for alpha particles in oxygen the relative total ionization as compared with air is 1.09 (38). This will give 29.5 e.v. expended per ion pair in oxygen. From the total reaction the number of molecules formed or decomposed can be determined. The calorimetric measurement gives the energy in calories. The energy expended in volts per molecule can then be calculated, and a comparison with the expenditure per ion pair gives a value for the number of molecules reacted per ion pair. In the case of ammonia gas the total ionization relative to air was taken to be 0.95, and it will take 33.9 e.v. to produce one ion pair in ammonia gas. The mean energy per electron was 48,000 e.v., and such an electron decomposed 1690 molecules, so that 28.4 e.v. of energy was expended per molecule. The M/N ratio is calculated to be 1.2 as noted above.

Ammonia synthesis. Since it is possible to synthesize ammonia gas from its elements by alpha-ray activation (39, 40) ($M/N = 0.25$, approximately), and (41) in glow discharge, it was a foregone conclusion that the synthesis should also be possible with cathode rays. Busse and Daniels (26) attempted it but obtained inconsistent results. However, Gedye and Allibone (42) successfully studied this reaction; they found that not only ammonia but also hydrazine is formed when hydrogen-nitrogen gas mixtures are rayed with cathode rays. They point out that outgassing the reaction vessel by bombarding the walls in vacuum is very important for success in these experiments. Ammonia and hydrazine were identified by the usual chemical methods. The hydrazine yield was of the same order of magnitude as the ammonia yields. The reaction is of low efficiency; 300 e.v. of energy are expended per molecule of ammonia formed, which gives a yield of 0.1 molecules per ion pair ($M/N = 0.1$). This low value is of the same order of magnitude as the results of other methods.

Polymerization reactions. With acetylene in electric discharge polymerization has been observed by de Wilde and Thenard (43, 44), and since then it has been studied with all kinds of activating agents. It was therefore to be expected that fast cathode rays should be able to produce the polymer as has been shown by Coolidge (45) and by McLennan, Perrin and Ireton (46). These investigators followed the polymerization by noting the pressure drop in a vessel fastened to the window of the cathode-ray tube. No reaction was noted below 85,000 volts, which is the potential necessary to drive the electrons through the window. For higher voltages, reaction took place, and at any given voltage the rate of pressure drop was proportional to the pressure, the change being apparently monomolecular. The velocity constant is directly proportional to the applied voltage. The product is a yellow solid, called "cuprene," which has no vapor pressure, and further bombardment with cathode rays did not affect it. Its specific gravity is 0.97, and its index of refraction is 1.625 for yellow light. The number of electrons escaping through the window were measured for various applied voltages. An interesting calculation was made by considering the number of molecules which will be hit by an electron while crossing the reaction vessel. It was found that an electron crossing 27 cm. of acetylene gas at 12.5-cm. pressure will impinge upon 3.77×10^4 molecules. The molecular diameter of acetylene is taken to be 10^{-8} cm. From the known volume of the reaction vessel (805.5 cc.) and from the measured pressure drop (0.4 mm. per min.) it was found that 1.1×10^{19} molecules disappeared per minute. The current just outside the window was 6.0 microamp., which is equivalent to 2.26×10^{15} electrons per minute. Therefore 4.9×10^3 molecules of acetylene were removed per electron crossing the vessel. This number is of the same order as the number of collisions between one electron and the acetylene molecules. However, if one compares the reaction with the similar condensation by alpha rays assuming 100% of the collisions to ionize it is seen that the number of ionizing collisions need only be 1/20 as efficient in order to produce the same amount of reaction.

Bombardment of ethylene results in a fall of pressure, according to McLennan and Patrick (47). A liquid product is formed. The rate of pressure drop increases with the initial pressure, but not linearly, which means that the reaction order is greater than unity, indicating that more than two molecules are involved in the reaction. The effect of cathode rays upon ethylene is intermediate between the effects on methane and acetylene. Acetylene is polymerized, and the resulting product is not affected by fast electron bombardment. Methane is acted on slowly, giving hydrogen and ethane, which are gaseous, and ethane at least can be changed further by cathode rays. Ethylene gives a liquid product which can be affected further by bombardment giving hydrogen, saturated hydrocarbons and acetylene.

The well-known polymerization of gaseous formaldehyde to paraldehyde is greatly hastened by cathode-ray treatment. The solid polymer is decomposed by a complicated action into hydrogen, carbon dioxide, carbon monoxide and methane.

Condensation of hydrocarbons. From the effect of electric discharge on hydrocarbons as discussed in Chapter VII it follows that cathode rays must cause similar changes, as indeed has been found by several investigators. In connection with the problem of the deterioration of electric power cables (page 323), liquid hydrocarbon oils have been studied under cathode-ray bombardment by Schoepfle and Connell (48), who, using a Coolidge tube, obtained condensation and polymerization analogous to the similar actions when produced by electrical discharge and by radon treatment. Large amounts of gas, mainly hydrogen, were obtained from saturated and only small amounts from unsaturated oils under electrical bombardment at 170,000 volts and 0.3 milliamp. Besides these gaseous products there is formed a solid material resembling the wax from power cables (page 323). This wax showed a higher carbon to hydrogen ratio (7.6) than the original cable compound (6.81). It absorbed oxygen readily from the air.

In order to study this problem of cable failure from a more fundamental point of view, Schoepfle and Fellows (49) investigated the action of cathode rays on pure hydrocarbons. They determined the amount and composition of the gaseous products. As with the oils studied earlier, so with pure liquids the saturated hydrocarbons gave larger volumes of gaseous decomposition products than did unsaturates. Hydrogen and saturated hydrocarbon gases make up most of the yield. Aromatic hydrocarbons give practically no gases under electron bombardment. Branched-chain compounds, as might be expected, yield more methane and they also give larger amounts of other hydrocarbons of the saturated series than do straight-chain structures. The volume of gas obtained was largest with hexane (57 cc. N.T.P.) and decreased with increase in molecular weight. *n*-Tetradecane gave only 34 cc. (N.T.P.) of total gas under the same treatment with high-speed electrons. Three isomeric octanes yielded about the same amount of gas showing that branching has no great influence. Cycloparaffins also produced large amounts of gas, corresponding to straight-chain saturates. Compounds of an intermediate character would behave in a manner indicating that the aromatic character predominates, i.e., not as much gas is evolved as might be expected. It appears that the hydrogen produced in the condensation may be taken up by unsaturated compounds with which it is in contact when liberated in the active form.

Concerning the composition of the gaseous products it is noted that hydrogen increases relative to methane and saturated hydrocarbons, with increasing molecular weight of the saturated liquid hydrocarbons studied. The isomeric octanes gave the same amount of gas but the composition was quite different. The branched-chain compounds produced relatively more methane and saturated gaseous hydrocarbons. These relations and findings can be studied and derived from the material in Table 10.

A set of simple paraffin hydrocarbons (methane to butane) were exposed to the rays of a Slack tube by Lind, Marks and Glockler (50). The only product of the decomposition identified was hydrogen. The experimental set-up is shown in Fig. 47*a*, and the reaction vessel in Fig 47*b*. The ratio of hydrogen formed per electron was calculated from the gas collected and the current crossing the tube. For the four hydrocarbons studied, on the average, 10 hydrogen molecules were produced per electron. If only 1% of these electrons cross the reaction vessel, then 1000 hydrogen molecules are formed per electron, and since for every hydrogen molecule most likely 2 hydrocarbon molecules are decomposed, it follows that roughly 2000 hydrocarbon molecules decompose per electron.

From the energy loss suffered by an electron in crossing the gas contained in the reaction vessel, it is possible to estimate that one electron may produce about 1000 ion pairs. So it appears that 2 molecules of hydrocarbon react per ion pair, and this result points to an analogy between cathode-ray- and radon-activated reactions.

One of the original objects of the present work was to investigate whether the relative amounts of chemical reaction produced by high-speed cathode rays in the four hydrocarbon gases investigated might be a measure of their relative stopping powers for swift cathode rays. The reasoning was as follows:

When alpha particles act on the same four hydrocarbons the amount of reaction per ion pair remains constant, but the amount of action per unit of path of the alpha particle which entirely traverses the gas is in proportion to their relative stopping powers, or about as 1 : 1.8 : 2.5 : 3.2

TABLE 10

EFFECT OF CATHODE RAYS ON HYDROCARBONS

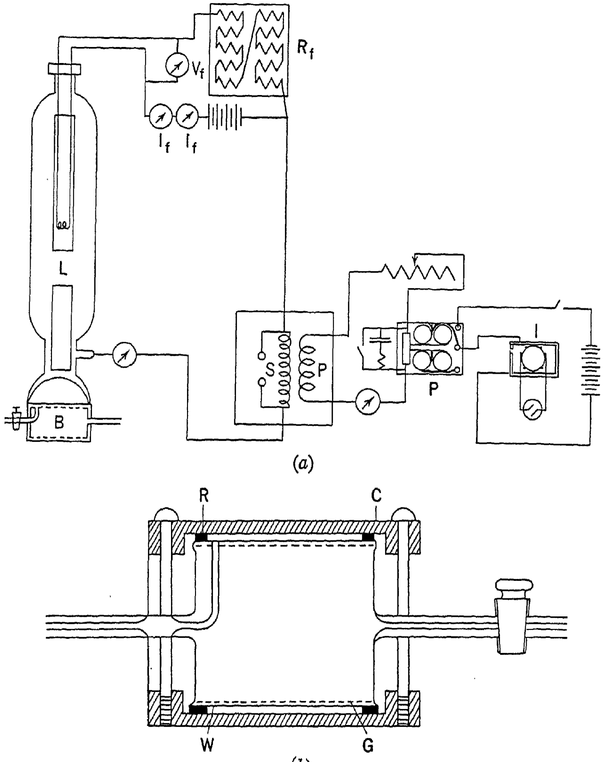
C. S. Schoepfle and C. H. Fellows, J. Ind. Eng. Chem. **23**, 1396 (1931)
(170,000 Volts, 0.3 Milliamp.; Coolidge Tube; Sample 72 mm. from Window; No Air Present)

Hydrocarbon:	Total gas produced in 30 min. (cc. N.T.P.)	Volatility in liquid air		Composition of volatile portion		Composition of total gas	
		Volatile portion %	Non-volatile portion %	H_2 %	CH_4 %	H_2 %	CH_4 %
Paraffins:							
n-Hexane	57.6	72.1	27.9	91.9	7.3	66.3	5.3
n-Heptane	51.4	80.8	19.2	95.1	4.8	76.9	3.9
n-Octane	48.3	81.7	18.3	96.4	3.4	78.8	2.8
n-Decane	41.6	81.8	18.2	96.5	2.6	78.9	2.1
n-Tetradecane	34.9	93.1	6.9	97.8	1.7	91.1	1.6
2,5-Dimethylhexane	49.8	53.8	46.2	78.2	21.5	42.1	1.6
2,2,4-Trimethylpentane	50.3	51.8	48.2	67.8	29.3	35.1	15.2
Olefins:							
Caprylene	16.4	75.0	25.0	92.3	6.5	69.2	4.8
Diisobutylene	20.8	55.3	44.7	70.5	29.2	39.0	16.1
Cycloparaffins:							
Cyclohexane	45.8	91.0	9.0	97.7	1.4	88.9	1.3
Methylcyclohexane	39.2	87.0	13.0	95.2	3.6	82.8	3.1
Decahydronaphthalene	37.2	98.8	1.2	99.5	......	98.2	
Cycloölefins:							
Cyclohexene	18.8	61.0	39.0	93.0	6.0	56.7	3.7
1-Methylcyclohexene	14.0	80.7	19.3	92.0	6.5	74.2	5.3
Pinene	5.5	74.9	25.1				
Limonene	7.5	78.9	21.1				

Total gas evolved from aromatic hydrocarbons in 30 min. (cc. N.T.P.)

Benzene	2.2	Phenanthrene	0.5
Toluene	2.7	Diphenyl	<0.5
Hexamethylbenzene	7.5	Diphenylmethane	0.8
p-Cymene	3.5	Triphenylmethane	0.9
Naphthalene	<0.5	Tetrahydronaphthalene	2.6
α-Methylnaphthalene	0.7	Phenylcyclohexane	2.3
β-Methylnaphthalene	0.9	90% benzene and 10% cyclohexane	3.2
Anthracene	<0.5		

for methane, ethane, propane and butane, respectively. If then sufficiently swift cathode rays could be obtained to go entirely across the reaction cell in approximately straight lines, possibly relations similar to those for the alpha particles would be derived. The experimental results do not indicate such a relation, and it remains to be shown whether this finding is simply due to real lack of such proportionality or whether the experimental errors have been too great to discover it. The calculations on the energy of the cathode rays do not indicate lack



(*a*)

(*b*)

FIG. 47.—(*a*) Slack-Lenard cathode-ray tube and electrical set-up: SP = high-tension transformer; R_f, V_f, I_f = filament circuit; IP = interrupter and contact for primary transformer circuit; B = reaction bulb; L = Lenard tube. (*b*) Reaction bulb detail: G = grid; R = washer; W = aluminum window; C = clamp. Lind, Marks and Glockler, Trans. Am. Electrochem. Soc. 59, 137 (1931).

of energy either before reaching or on passing across the reaction tube. Methane had also been rayed by McLennan and Glass (34), who found that electrons from a Coolidge tube (136 kv., 0.13 amp.) produced very little pressure change in methane at 20-cm. pressure but that there had been some reaction, because after exposure the gas contained 16% of hydrogen, 14.3% ethane, the rest being unaltered methane. No tarry or oily matter was deposited on the walls of the reaction vessel. In moist methane small amounts of carbon dioxide and carbon monoxide were formed, but the decomposition into hydrogen and ethane proceeded to the same extent.

Oxidation of methane. Alpha-ray activation causes complete oxidation of methane to carbon dioxide and water (51). The same action may well be expected upon exposure of the above gas mixture to fast electrons. McLennan and Glass (34) found this to be the case. The water produced contained formic acid. They also obtained carbon monoxide and hydrogen. The relative proportions of these products do not vary greatly under a wide variation of experimental conditions. The formic acid may be produced from the carbon dioxide and hydrogen. The striking result is the incomplete nature of the oxidation, and the action of the cathode rays appears to show the initial stages of the combustion, because electrons do not ionize as effectively as the alpha rays from radon.

Effect on alcohols, aldehydes and ketones. Such substances have been studied under the influence of cathode rays by McLennan and Patrick (47). Acetaldehyde and acetone both yield condensates, and gaseous products are formed: CO_2, C_2H_2, C_2H_4, CO, H_2, CH_4 and C_2H_6. When these products are compared with the results of similar reactions on formaldehyde it appears that the relative value of CO to CO_2, the amounts of ethane from aldehyde and acetone and various other intercomparisons show a reaction picture as is to be expected from the structure of these molecules. Similarly the action on methyl and ethyl alcohols was studied, and it was found that a great deal of hydrogen is evolved. It appears that the action consists in a dehydrogenation with subsequent decomposition of the aldehyde formed. The gaseous products are similar to the ones obtained from aldehyde.

As far as the chemical effects of cathode rays are concerned it appears that most of these reactions can be carried out in an ordinary ozonizer with greater ease and comfort. Ozone can be produced more efficiently; hydrocarbons can be condensed satisfactorily; polymerizations are equally possible. Whenever the fast electrons are required outside their generating tube, as in the study of biological systems (52–55), then the cathode-ray tube is the only means of producing them. It may be expected that in the course of time cathode rays may rival radium and its radiations.

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CHAPTER V

REACTIONS CAUSED BY ELECTRONS OF KNOWN SPEED

Introduction. It has been shown in previous chapters that the chemical reactions occurring in ozonizers, luminous discharges, sparks or arcs are all due to excitation or ionization produced by electrons of varying speed. The actual potential differences employed are sometimes very large and, depending upon the pressure, there may be present, in such devices, electrons with speeds ranging from zero to many hundreds of volts. For the study of the mechanism of such activated reactions it is of great interest to know just what minimum energy or velocity an electron should possess in order to produce a certain type of activation. If ions alone serve as activating centers then it would seem reasonable that a given reaction should set in at the ionization potential of the gas in question. However, it may also be possible that excited or resonated atoms or molecules can serve as reacting centers. Furthermore, metastable states may be very efficient in promoting the activation of certain chemical reactions on account of their long life. In the last two cases the impacting electrons need only reach some resonance potential of the atom or molecule. In either case a study of chemical reactions with electrons of known speed will give the information desired. It will be seen that such reactions can be understood completely on the basis of the energy states of molecules, for the interaction of electrons and molecules is governed by quantum relations. These reactions will then be interpreted on the basis of energy level diagrams of molecules as obtained from their band spectra. The present case of interaction of electrons of known speed and molecules is quite analogous to the photochemical activation of chemical reactions. In order that radiation of a given color may cause photochemical activation, the radiation must be of such a wave length that it can be absorbed by the reacting system. Similarly electrons must have certain well-defined speeds before they can transfer their energy to molecules or atoms, so that they may be brought into a reactive state.

The best way of obtaining electron streams of known speed is to use the thermionic emission of hot filaments. The presence of the hot filament limits at once the number of systems that can be studied, because the molecules must be stable at the high temperature of the filament and the reaction products must be removed quickly to avoid their thermal decomposition. It is very important to keep in mind this possibility of thermal reaction; if it cannot be avoided, allowance for its presence must be made. One great advantage in the use of electron streams as activating agents of chemical change lies in the fact that electrons of any desired speed can readily be produced by varying the accelerating voltage applied to them, so that the whole spectrum of electron energies can be covered. This is an advantage which the method has over photochemical activation where radiations of various frequencies cannot be produced so easily and at will. Also the electron streams can be made fairly monochromatic since usually the initial velocity distribution varies by only a fraction of a volt.

Dissociation of hydrogen. One of the simplest chemical reactions that has been studied with slow electrons is the dissociation of diatomic molecules. The heat of dissociation of hydrogen molecules was first determined by Langmuir (1). The value accepted at present is 100,000 cal. per mole (2). It may then be expected that electrons of 4.34 e.v. energy could dissociate hydrogen molecules on impact, provided that they can transfer this energy to the molecules upon collision. However, it will be seen that such slow electrons have no effect on hydrogen molecules. Although they possess the necessary kinetic energy relative to the hydrogen molecule they cannot transfer it, hence the collisions are elastic ones. Evidently the mere possession of sufficient energy by the impinging electron is not adequate to cause dissociation. The further condition is that the interaction is one governed by quantum conditions. The experimental arrangement employed in these investigations will now be considered.

The apparatus used in such studies is shown diagrammatically in Fig. 48. Electrons are liberated from the hot filament *F* and they are accelerated towards the grid *G*, because they fall through the potential V_a applied between filament and grid. The grid is positive towards the filament. The region between filament and grid is made small enough so that it is less than the mean free path of an electron at the gas pressure used. In the space between the grid and the plate the electrons make impacts with the gas molecules present. At the proper voltage such impacts will lead to dissociation of the molecules, which can be detected by a pressure decrease, if it is possible to remove the resulting atoms. In the case of hydrogen Langmuir (1) has shown that the atoms may be frozen out on glass surfaces at liquid-air temperatures. The advent of dissociation is then determined by noting the pressure decrease as a function of accelerating voltage applied to the reaction tube which is immersed in liquid air. Hughes (3) showed that electrons must reach a velocity of 13.5 e.v. before they can dissociate hydrogen. Similar experiments were carried out by Glockler, Baxter and Dalton (4). These investigators had present near the impact region a copper oxide surface which removes hydrogen atoms by reduction and formation of water. The water can be frozen out in a side trap by means of liquid air. Measurements, in the same tube, of the critical potentials of hydrogen by the Franck and Hertz (5) method showed a critical potential at 11.6 e.v., and reaction was first noticed when the electrons had 11.4 e.v. of energy. The same voltage was also found by Hughes and Skellett (6) when they studied the effect of electrons on hydrogen using liquid air as an agent to freeze hydrogen atoms upon the glass surfaces of the reaction tube. They also noted that, with both 100-volt and 20-volt electrons, the rate of pressure decrease is directly proportional to the pressure. Hence the dissociation of hydrogen molecules by electron impact cannot be a secondary effect, as, for example, the result of a collision between a neutral molecule and an excited one, for then the effect would vary as the square of the pressure.

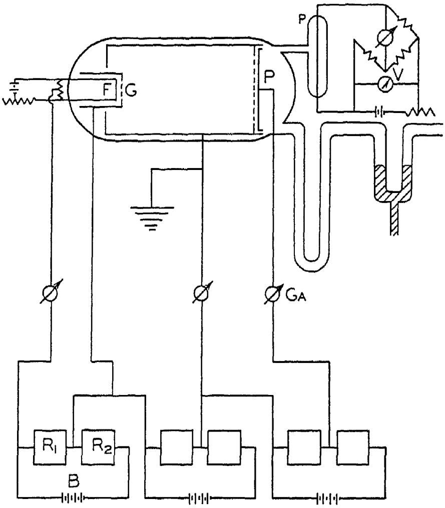

FIG. 48.—Apparatus and wiring diagram for the study of reactions by means of electrons of known speed. F = filament; G = grid; P = plate; p = Pirani gauge; Ga = galvanometer; R_1R_2 = potentiometer resistance boxes; V = voltmeter; B = batteries (20–30 volts). Glockler, Baxter and Dalton, J. Am. Chem. Soc. 49, 58 (1927).

The following interactions are possible between electrons of definite speeds and hydrogen molecules (see also Ref. 34):

$H_2(^1\Sigma_g{}^+) \rightarrow 2H(^3\Sigma_u{}^+;\ \text{kinetic energy})$ − 11.6 e.v.*
$H_2(^1\Sigma_g{}^+)\quad H_2{}^*(^1\Sigma_u{}^+,\ \text{excited})$ − 11.4 e.v.
$H_2(^1\Sigma_g{}^+)\quad H_2{}^+ + E^-$ − 15.34 e.v.
$H_2(^1\Sigma_g{}^+)\quad H + H^+ + E^-$ − 17.84 e.v.

The electron velocities mentioned are the minimum energies electrons must have in order to produce the changes indicated. Faster electrons may still have similar effects with appropriate efficiencies, and the resulting particles (atoms, ions, etc.) will separate with relative kinetic energy, as has been shown by Lozier (7).

These interactions between an electron and a hydrogen molecule can be understood only on the principles of quantum mechanics, and it is necessary to consider the energy diagram of the hydrogen molecule (8, 35) (Fig. 49). It is seen that hydrogen molecules exist in the normal state designated by $^1\Sigma_g{}^+$. The first possibilities of excitation of interest here are the various vibrational states of the normal molecule which finally lead to dissociation. Since slow electrons of 4.34 e.v.

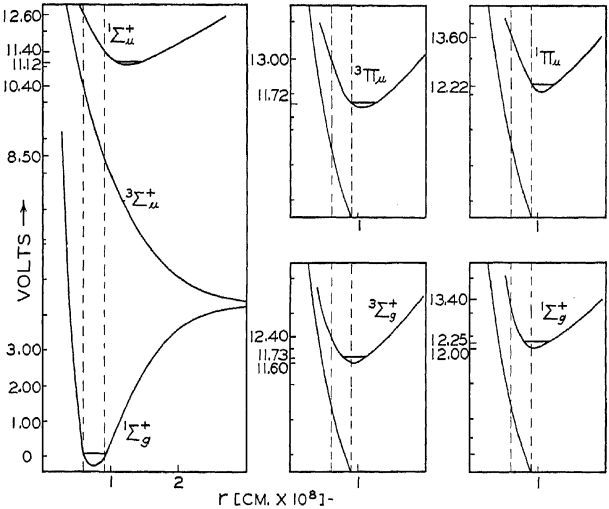

FIG. 49.—Energy level diagram of the hydrogen molecule. R. S. Mulliken, Rev. Mod. Phys. 4, 46 (1932).

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* (11.6 e.v. (4); 8.4–10.4 e.v. (8); 8.4–12.0 e.v. (35).

energy cannot dissociate hydrogen molecules, it is seen that such electrons cannot transfer their energy to the vibrational states. However, when electrons reach a speed corresponding to 11.6 e.v. it is seen from the energy diagram that they can change a normal molecule ($^1\Sigma_g{}^+$) to the repulsive state $^3\Sigma_u{}^+$. These excited molecules can explode spontaneously and separate into two hydrogen atoms of high kinetic energy. These atoms are the ones that react with the copper oxide surface to form water, or they are frozen out on the glass wall, producing the pressure decrease observed. In the present case another possibility exists, namely, that hydrogen molecules are transferred from the normal state to the excited state ($^1\Sigma_u{}^+$) by electrons of 11- to 12-e.v. energy. If the reaction happens via this state, then these excited molecules must dissociate upon impact with normal molecules, or if they reach the wall they must be able to dissociate there or react with copper oxide as the case may be, so as to produce the observed pressure decrease. Between the lowest excitation potential (11.4 e.v.) and the ionization potential of hydrogen molecules, several other energy states are known which most likely will serve as activated states. They have not been investigated in detail. At the ionization potential the rate of pressure drop increases, showing that the new ionic species formed at the higher potential also can serve in some way as an activating agent in these reactions. The important results of these experiments lie in the fact that electrons of definite low speed can make molecules reactive. This means that, in any of the devices used for the study of electrochemical gas reactions, a much higher voltage is employed than is necessary for the reaction which it is desired to produce. Of course this extra voltage drop is needed to create the ionization which in turn maintains the discharge.

It is furthermore of great interest to note that molecules need not be *ionized* before they can react. In the case studied, the hydrogen molecules needed only 11.4 e.v. for activation, which placed the normal ($^1\Sigma_g{}^+$) molecules into the ($^3\Sigma_u{}^+$) repulsive state. To be sure, this state is somewhat exceptional and does not correspond to a resonance potential in the ordinary sense. However, it seems plausible that any energy-rich (i.e., excited atom or molecule) will be in a more reactive mood than a normal one. Furthermore, it would appear that metastable states (9) should play a very prominent part in such activation reactions, on account of their long lives. Normal, excited and metastable atoms, excited and metastable molecules and normal, excited and metastable radicals may be expected to play their part in reactions taking place in discharge tubes, and all these species must be considered in a general scheme of reaction mechanism.

Mercury-sensitized activation of hydrogen. Hydrogen molecules have been dissociated by electrons of known speed using mercury atoms as a sensitizing agent by Glockler and Thomas (34) (Figs. 50 and 51). These reactions are analogous to the photochemical decomposition of hydrogen using λ = 2537Å and mercury atoms (Cario and Franck experiment). As we have seen, electrons must have about 11.7 e.v. of energy before they can bring hydrogen molecules into a reactive state. However, when mercury atoms also are present in the reaction chamber one would predict that the hydrogen gas should become reactive at an electron speed of 4.9 e.v., because such electrons

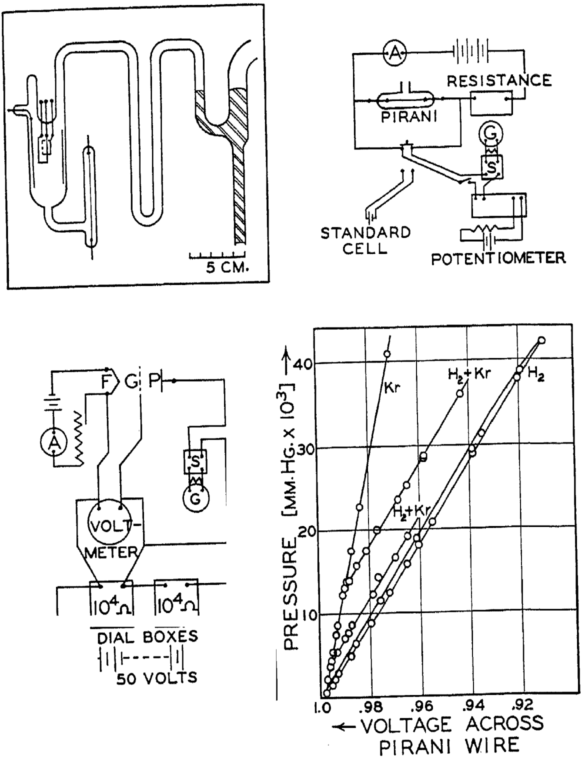
5 CM.
A
RESISTANCE
PIRANI
G
S
STANDARD CELL
POTENTIOMETER
F
G
P
A
S
G
VOLT-METER
$10^4\Omega$
$10^4\Omega$
DIAL BOXES
50 VOLTS
PRESSURE [MM.HG. x 10^3] →
40
30
20
10
Kr
H_2+Kr
H_2
H_2+Kr
1.0
.98
.96
.94
.92
← VOLTAGE ACROSS PIRANI WIRE

FIG. 50.—Controlled electron reactions. Reaction tube; electrical connection of reaction system and Pirani gauge; Pirani gauge calibration curves. Glockler and Thomas, J. Am. Chem. Soc. 57, 2352 (1935).

can excite mercury atoms to the 6^3P_1 state and they in turn can transfer their internal energy to the hydrogen molecules by impacts of the second kind. Experiment showed, however, that the short-lived radiative states of mercury (4.9 and 6.7 e.v.) and the well-known metastable states ($6^3P_{0,2}$) are not efficient or too short-lived to cause reaction. However, electrons of 7.7 e.v. energy initiate the dissociation of hydrogen in the presence of mercury:

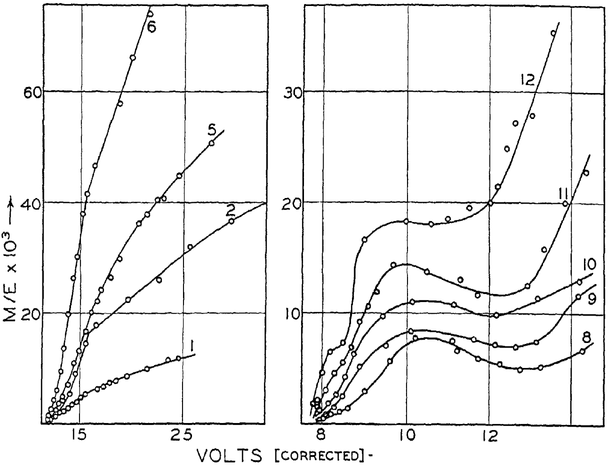

FIG. 51.—Hydrogen decomposition by controlled electrons. Non-sensitized reaction and sensitized by mercury atoms. Glockler and Thomas, J. Am. Chem. Soc. 57, 2352 (1935).

$$E^-(7.7\text{ e.v.}) + \mathrm{Hg}(6^1S_0) - \qquad\qquad + E^-(\text{zero e.v.})$$

$$\mathrm{Hg}(7^3S_1) \rightarrow \mathrm{Hg}(6^3P_{0,2}) + \qquad\qquad \text{or } 4047\text{Å})$$

$$\mathrm{Hg}(6^3P_{0,2}) + H_2(^1\Sigma_g^+) \rightarrow \text{H (atoms)} + \mathrm{Hg}(6^1S_0)$$

$$2\text{H(atoms)} + \text{CuO(solid)} \quad H_2O\text{(liq.)} + \text{Cu(solid)}$$

Dissociation of nitrogen. This reaction was studied by Hughes (3), who found that 17.8 volt electrons are able to affect nitrogen molecules in such a way that a new species formed can be frozen out on the glass walls of the reaction tube at liquid-air temperatures or removed by adsorption even at room temperatures, producing a pressure decrease in the reaction vessel.

The following interactions between nitrogen molecules and electrons have been studied (8, 10, 11, 12).

$$-\ 8.5\ \text{e.v.}$$

$$N_2(^1\Sigma_g{}^+) \rightarrow N_2{}^* \text{ (excited)} \qquad -\ 8.4\ \text{e.v.}$$

$$N_2(^1\Sigma_g{}^+) \rightarrow N_2{}^+ + E^- \qquad -\ 15.7\ \text{e.v.}$$

$$N_2(^1\Sigma_g{}^+) \rightarrow N + N^+ + E^- \qquad -\ 22.9\ \text{e.v.}$$

$$N_2(^1\Sigma_g{}^+) \rightarrow N^* \text{ (metastable)} + N^+ + E^- \qquad -\ 25.9\ \text{e.v.}$$

$$N_2(^1\Sigma_g{}^+) \rightarrow N^* \text{ (P state)} + N^+ + E^- \qquad -\ 33.2\ \text{e.v.}$$

$$N_2(^1\Sigma_g{}^+) \rightarrow 2N^+ + 2E^- \qquad -\ 37.4\ \text{e.v.}$$

The first pressure decrease was observed at 17.8 e.v., so that electrons must have a greater energy than corresponds to the heat of dissociation before they can change the nitrogen molecules into a condensible form. From the reactions noted above it seems most likely that the primary act is the formation of mole ions and that these ions upon collision separate into nitrogen atoms and atomic ions. If nitrogen atoms are condensible on glass surfaces, the experiments described can be understood completely:

$$N_2(^1\Sigma_g{}^+) \rightarrow N_2{}^+ + E^- - 17\ \text{e.v.}$$

$$N_2{}^+ + (P,W) \rightarrow N^+ + N + (P,W)$$

In the second equation (P,W) stands for the wall or a particle such as normal nitrogen molecules with which the nitrogen mole ion makes collisions. It should be noted that there will have to be available about 6 volts of relative kinetic energy in such collisions in order to produce the atom and atom ion. In the impact region between grid and plate the gas is under quite a temperature gradient. The filament is at about 1500° C., and the wall is at liquid-air temperature. The mean temperature of the region is somewhere near room temperature. Under these conditions not many impacts between molecules will have such high relative kinetic energy as is represented by 6 e.v. If the nitrogen mole ion reaches the wall it is conceivable that its neutralization will furnish the energy for subsequent dissociation into atoms. More dissociation occurs at higher electron energies, but especially marked increases of reaction have not been observed at the energies corresponding to the reactions noted above.

Activation of oxygen. Dalton (13) studied the reaction between oxygen molecules activated by electrons of known speed and a solid carbon surface. He also measured critical potentials of oxygen and found two values: 7.9 and 10.6 e.v. The second potential depended in a peculiar way upon the pressure of oxygen in the vessel. He followed the reaction in the customary way by noting the pressure decrease as a function of accelerating voltage. The activated oxygen molecules react with the carbon lampblack deposited on the grid to form carbon dioxide. This product was identified in the usual manner. The carbon deposit was placed as far away as possible from the hot filament so as to reduce thermal reaction. He found increased pressure drops at the critical potentials noted above. The first potential at about 8 volts he identified as the resonance potential of oxygen which had been known previously (14). The second potential at 10.6 e.v. does not appear to belong to the oxygen molecule as will be seen from the energy level diagram of oxygen given in Fig. 52. Dalton suggested that it may be due to carbon dioxide, which has a critical potential at 10 e.v., according to MacKay (15). This would account for the variation with pressure since at low oxygen pressures the carbon dioxide would diffuse rapidly to the liquid-air trap whereas at higher pressures its removal would be retarded. Moreover, this potential would not be found in pure oxygen gas free from carbon dioxide, but it would suppose that collisions between carbon dioxide molecules and electrons are very much more efficient than between oxygen molecules and electrons. Other investigations reported below do not show this second critical potential.

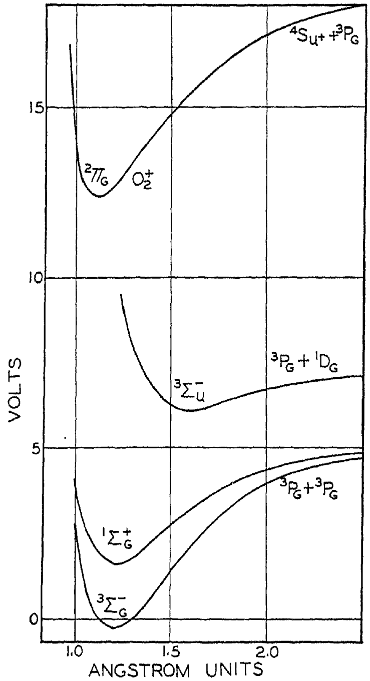

FIG. 52.—Energy level diagram of the oxygen molecule. Mulliken, Rev. Modern Phys. 4, 46 (1932).

Wansbrough-Jones (16) studied the effect of slow electrons on oxygen molecules and especially the question of ozone formation. In a closed system he noted small pressure drops due to adsorption of some active species produced by electron collision, but no ozone was formed up to 60 volts applied potential. Any ozone found is decomposed again at the metal surfaces of the apparatus. However, in a flow system he was able to find ozone by adsorption in concentrated sulphuric acid. The lowest potential at which ozone could be formed was 25 e.v. between filament and grid, and no ozone was obtained at pressures below about 1 mm. of oxygen. On account of the high potential needed it appears that ions are necessary for the mechanism of ozone production, and the fact that low pressures are unfavorable for ozone formation led Wansbrough-Jones to suggest that an *excited* ion of short life (10^{-7} sec.) is required to form ozone by collision with ordinary oxygen molecules.

Henry (17) investigated the activation of oxygen by electron impact, using a four-electrode tube which also allowed him the determination of critical potentials by the usual methods. He showed that ozone was produced at 28 volts, by determining the absorption spectrum of the gas after reaction. At lower potentials he measured the pressure decrease and surmised that ozone was formed there also, without, however, offering direct proof. Although he found critical values at 8.9, 14.7, 17.9 and 21.2 e.v. and noted changes in pressure drop at 9.0, 17.4, and 21.2 e.v. it cannot be claimed that ozone is actually formed at these potentials, for he was unsuccessful in showing its presence below 28 volts. If ozone was formed, it was present in such small concentration that it could not be detected by the means employed. From the pressure drops noted it is evident, however, that some new form of oxygen is produced which can be frozen out on the glass walls of the vessel by means of liquid air.

The activation of oxygen was further studied by Glockler and Wilson (18), who used a mercury surface and also the glass wall of the reaction tube to catch any condensible species of oxygen produced by electron impact with ordinary oxygen. Pressure drops were noticed without accelerating fields, and such zero rates of pressure drop due to thermal effects of the filament were subtracted from the rates, with fields on, in the usual manner. They found very small pressure changes with slow electrons (3–8 volts of energy) and increased reaction at 8 e.v.

This behavior must be now interpreted on the basis of the energy level system of molecular oxygen (8). The following interactions between electrons and oxygen molecules are known (19):

$$
\begin{aligned}
&O_2(^3\Sigma_g{}^-) \rightarrow O_2(^1\Sigma_g{}^+) && -1.62\,\text{e.v.}\\
&O_2(^3\Sigma_g{}^-) \rightarrow 2O(^3P_g) && -\ \ 5.1\,\text{e.v.}\\
&O_2(^3\Sigma_g{}^-) \rightarrow O(^3P_g) + O(^1D_g) && -\ \ 8.2\,\text{e.v.}\\
&O_2(^3\Sigma_g{}^-) \rightarrow O_2{}^+(^2\Pi_g) + E^- && -12.5\,\text{e.v.}\\
&O_2(^3\Sigma_g{}^-) \rightarrow O(^3P_g) + O^+ + E^- && -18.6\,\text{e.v.}\\
&\qquad\qquad\qquad\qquad\quad + O^+ + E^- && -20.5\,\text{e.v.}
\end{aligned}
$$

The first reaction corresponds to the transfer of normal oxygen molecules ($^3\Sigma_g{}^-$) to a metastable state ($^1\Sigma_g{}^+$) of molecular oxygen. If 1.62 volt electrons can transfer their energy to normal molecules and bring them into this metastable state and if such metastable molecules can react with a mercury surface, then it is understandable that a pressure drop may be produced at small electron energies (3–5 e.v.). It is further necessary to assume that the heat of activation for the reaction of metastable oxygen molecules ($^1\Sigma_g{}^+$) with a solid mercury surface is less than 1.62 e.v., which does not seem unreasonable. It should be noted that such metastable states are not found in hydrogen and nitrogen molecules and a similar reaction is not to be expected in these gases. The next transformation in order of energy required to produce it is the straight dissociation of oxygen molecules into two normal atoms, which requires 5.1 e.v. None of the investigators find any new reaction setting in at this electron voltage, and it appears that direct dissociation of oxygen molecules into normal atoms is not possible, as was the case with hydrogen and nitrogen. The next interaction, noted above, requires 8.2 e.v. in accordance with the Franck-Condon principle, and the result is a normal and excited atom of oxygen. Both Henry (17) and Glockler and Wilson (18) find increased pressure drops when this accelerating voltage is reached, and it is evident that the resulting atomic species can be adsorbed readily at cold glass surfaces and that they can react with a cold mercury surface. At the ionization potential of the molecule (12.5 e.v.) corresponding to the production of mole ions no remarkable increase in reaction rate is noted by both investigators, and it appears that this new ionic species is not any more efficient in adsorption and reaction than are the atoms. The last two reactions mentioned above involve again the production of atoms either in the normal or an excited state and atomic ions. Both lead to greater reaction, according to Henry.

The production of ozone as found by Wansbrough-Jones and Henry seems to require a potential of 25 e.v. It may, of course, happen at lower potentials with such low efficiency that it has not been possible to demonstrate its occurrence. The behavior of oxygen under slow electron bombardment has also been studied by Nekrasov and Stern (32), who consider metastable O_2 molecules even more important than did Glockler and Wilson (18).

Ammonia synthesis. Hiedemann (20) reported very briefly on the synthesis of ammonia from nitrogen and hydrogen. The mixture of the two gases in the proportion necessary to produce ammonia was introduced into a tube similar to the apparatus described above. The electrons were given a few volts higher than the ionization potential of the two gases, and the presence of ammonia was proved by Nessler's reagent. The formation of ammonia is not due to catalysis, for at 2 volts no ammonia formation occurred and a little ammonia was formed just below the ionization potentials of nitrogen and hydrogen. Andersen (21) gives a more detailed account of similar experiments, showing that ammonia can be produced by slow electrons. Either gas alone did not form a new substance absorbable in concentrated sulphuric acid, whereas from their mixture gases disappeared under the same conditions, producing a pressure drop in the reaction system. He also showed that the pressure decrease stopped as soon as one of the components of a non-stoichiometric mixture was used up. Ammonia formation was found only after a potential of about 17.7 e.v. had been applied, corresponding to the ionization potential of the gases. The measurements of the accelerating voltages were not sufficiently accurate to decide which of the gases had to be ionized. For accelerating voltages higher than the ionization potential ammonia production increased. However, the curves obtained when plotting "ammonia production per electron" against voltage applied show a remarkable wave form with maxima at 22, 26 and 33 volts respectively. Electrons of these particular speeds seem to have greatest probability of causing activation of one of the reacting partners. Excess of nitrogen favors ammonia formation, so that not a stoichiometric mixture but one containing 90% nitrogen has the greatest reaction rate for a given set of conditions (constant current and voltage). From the experimental results obtained it is not possible to decide on a reaction mechanism. However, Andersen makes the interesting remark, that mere attachment of electrons to the molecules of hydrogen and nitrogen is unlikely to distort the fields of these molecules sufficiently to make them more reactive, because these two molecules are known not to possess very great electron affinities. Later Andersen (31) used photoelectrons and obtained no ammonia although hydrogen was cleaned up.

The next study of ammonia synthesis in point of chronological order was made by Storch and Olson (22), who used a two-electrode tube (filament and grid) in their work. They employed smaller voltage drops across the filaments and were thus able to measure the accelerating voltage applied to the electron stream with more accuracy. The wave form of the curves obtained by Andersen is explained by them as due to an absorption effect by nearly fully covered glass surfaces which show "fatigue" and can be avoided with freshly baked glass surfaces. In place of these wave curves they obtained steplike curves (Fig. 53), which, however, show the same critical voltages for reaction. The first indication of synthesis occurs at 17.0 e.v., and further increases in reaction are noted about every 4 volts. The formation of ammonia in sufficient amount to be detectable by Nessler's reagent does not occur unless an arc is present in the reaction zone. An increased nitrogen content favors the synthesis.

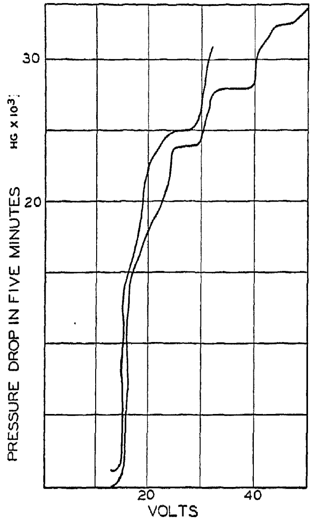

FIG. 53.—Ammonia synthesis by electrons of known speed. Storch and Olson, J. Am. Chem. Soc. **45**, 1605 (1923).

Another investigation of this synthesis was carried out by Caress and Rideal (23) in a three-electrode tube with either a tungsten or a platinum (BaO-covered) filament. With a very hot tungsten filament they found a catalytic reaction due to hydrogen atoms formed by thermal dissociation. This reaction is of no special interest here. With an oxide emitter no reaction was found below 17 e.v., and the rates of clean-up were small below this voltage. However, with hydrogen atoms present, produced by thermal dissociation at a hot tungsten filament, ammonia is formed at 13 e.v., owing to the interaction of an excited or ionized hydrogen atom and normal nitrogen molecules. Increased reaction is noted at 17 e.v. owing to N_2^+ ions and at 23 e.v. owing to N^+ ions.

Brett (24) sought to improve on earlier work on the synthesis of ammonia from its elements by electron impact, by using a better oxide emitter, thereby avoiding thermal dissociation of hydrogen, and by using a hot wire in place of a McLeod gauge for measuring the pressure. He obtained reaction beginning at 17.0 e.v., showing increases at 18.5, 20.5, 24.5 and 27.0 e.v., corresponding to the production of N_2^+, $H + H^+$, N_2^{*+}, $N + N^+$, $N^* + N^+$ and/or $H + H^+$ respectively.

From this summary of the work on ammonia synthesis by electron impact it is seen that it is not formed by such collisions in hydrogen-nitrogen mixtures below 17.3 e.v., which is the average value of four independent determinations. While the various authors either directly or by implication state that this voltage corresponds to the production of nitrogen mole ions, and that therefore this species is directly involved in the reaction mechanism of this synthesis, it is also seen that at present the ionization potential of nitrogen molecules is rather lower (15.7 e.v.). On the other hand, at 17.84 e.v. hydrogen molecules dissociate into hydrogen atoms and protons, and this value is much closer to the experimental one of 17.3 e.v. This raises the question whether this latter step is not the important one in the mechanism! Have these investigators been able to measure the initial velocity correction with sufficient accuracy so that the voltage values given are definite? Such points must be investigated more fully. It should be remembered that ammonia can be produced, according to Willey and Rideal (25), by the interaction of hydrogen atoms and normal nitrogen molecules. It must then be asked: why is no synthesis noticed at 11.4 e.v. when hydrogen atoms are produced by electron impact? The answer must be: these hydrogen atoms have large kinetic energies which may be unfavorable to any possible further reaction with nitrogen molecules, or the efficiency of hydrogen atom production at 11.4 e.v. is so small that the possible formation of ammonia has not yet been detected. This important reaction must be studied further in order to clear up these points. The increase in reaction at 23 e.v. is well established. Nitrogen atoms appear then for the first time, and they evidently can take part in a mechanism of reaction leading to synthesis of ammonia.

Reaction between oxygen and nitrogen. These two gases are known to react in the electric arc and in silent discharge with the formation of oxides of nitrogen, and it is of great interest to know the minimum velocities of electrons which can cause the combination of these two gases and furthermore which one of these two molecules will have to be activated. These questions were studied by Wansbrough-Jones (26). He found a slight thermal reaction catalyzed by the hot filament which was negligible when compared with the electron-activated reaction. Great care was exercised to make the rate of reaction reproducible; it was found to be governed by a number of factors: the age of the filament, the thickness of the oxide coating, the form of the arc, the adequacy of the baking-out and the pretreatment of the electrodes. Some of these factors are difficult to control. However, it was definitely established that no reaction occurred unless the electrons have a velocity of 17.0 e.v. The slight pressure drop obtained below this voltage is due to oxygen alone. Another well-defined break was found at 23.0 e.v., and at 30 e.v. a further rapid rise in reaction rate was noticed. It is especially to be pointed out that none of the increases of reaction rate correspond to critical potentials of oxygen. The two values found at 17 and 23.e.v. must be quite accurate, because the voltage scale was checked against the known critical potentials of oxygen, nitrogen and also helium. It seems then proper to identify the first point with the appearance of N_2^+ and the second point with the first appearance of N^+:

$$E^- + N_2^+ + O_2 \rightarrow 2NO, \quad \text{at } 17\,\text{e.v.}$$

$$E^- + N^+ + O_2 \rightarrow NO_2, \quad \text{at } 23\,\text{e.v.}$$

The product of reaction was NO_2, which was confirmed by obtaining a deep red color with an alcoholic solution of alpha-naphthylamine and sulphanilic acid.

Henry (27) studied the same case and found increased reaction at 16.8 and 23.1 e.v. He identified nitrogen dioxide as the product by measuring its absorption spectrum, and he proposes the same reaction mechanism as did Wansbrough-Jones.

Sodium azide. The decomposition of solid sodium azide was studied by Müller and Brous (28) by subjecting a thin film of the substance to bombardment by electrons of known velocity. The reaction was carried out in a vacuum using an oxide filament. The resulting nitrogen was identified by its critical potentials. Reaction sets in at 11.65 e.v., and further changes in reaction rate were noticed at the critical potential of nitrogen.

Reaction of carbon monoxide and hydrogen. It has been known that carbon monoxide alone decomposes in the electric discharge (see Chap. VII) to form carbon, carbon dioxide and carbon suboxide C_3O_2. Caress and Rideal (29) found the same reaction in the case of electron activation. They studied the rate as a function of the electron speed in the accepted manner and noted that 14 e.v. were needed before the decomposition commenced. Increased reaction occurred at 19 e.v. Breaks in the rate curve found at higher voltage were not very reliable.

The two gases reacted with no accelerating voltage on the tube in the presence of the hot filament which produces hydrogen atoms by thermal dissociation. Formaldehyde is the chief product. Three critical potentials of reaction were obtained at 14.3, 20.0 and 29.7 e.v.

under conditions where thermal dissociation was avoided. This could be done by using a special oxide emitter. They also attempted to study the effect of electrons on the thermal reaction due to hydrogen atoms and carbon monoxide, and they found that the combination between hydrogen atoms and carbon monoxide ions (CO^+) is more rapid than the reaction between atomic hydrogen and normal CO molecules. On the other hand, protons (H^+) are not appreciably more reactive than atoms, or else they were not furnished in sufficient number to contribute greatly to the reaction, which at 14.3 e.v. is thought to be

$$CO^+ + H_2 + E^- \rightarrow HCHO, \quad \text{at } 14.3\,\text{e.v.}$$

and the increase at 20.0 e.v. must mean that excited CO ions in the 2^2S state have greater reactivity:

$$CO^+(2^2S) + H_2 \rightarrow HCHO, \quad \text{at } 20.0\,\text{e.v.}$$

whereas an excited state known for CO molecules to occur at 16.8 e.v. does not accelerate the change. Nor does increased reaction take place at 24 e.v. where carbon monoxide molecules can be dissociated into carbon atoms and atomic oxygen ions, so that these species do not seem to enter into combination with hydrogen.

From the pressure decreases observed it appeared that some polymerization occurred during the electron activation in the gas phase. This would lead to the view that clusters of the type $(HCHO)_n$ were formed about the excited CO^+ ions (2^2S) on account of or in addition to the fact that these excited ions have a larger collision area than ordinary ones.

From the energy level system of the CO molecule it is known that excited states are possible at 6.0, 7.14 and 7.99 e.v. At 9.3 e.v. carbon monoxide molecules can be dissociated by electron impact into carbon atoms and negatively charged oxygen atoms, according to Tate and Lozier (11). Dissociation into atoms is possible at 9.3 e.v. Molecular singly charged ions appear at 14.0 e.v. Excited molecular ions appear first at 16.52 e.v. in the 2Π state and at 19.63 e.v. in the $^2\Sigma^+$ state. Dissociation into carbon atomic ions and negative atomic ions of oxygen is possible at 22.2 e.v. From these various possibilities it is seen that the processes chosen by Caress and Rideal are the only reasonable ones. It is of interest that negative oxygen atoms have no special reactivity towards hydrogen or carbon monoxide.

Decomposition of sulphur dioxide. The following reactions take place when sulphur dioxide gas is bombarded at low pressure (0.01 mm.

Hg) with slow electrons from a calcium-oxide-covered filament, according to Nekrasov and Schneerson (33):

$$SO_2 \rightarrow SO_2^+ + E^-, \qquad \text{at } 12.2 \pm 0.5 \text{ e.v.}$$

$$SO_2 \rightarrow SO^+ + O + E^-, \qquad \text{at } 15.7 \pm 0.5 \text{ e.v.}$$

The reaction is followed by pressure changes. Besides the critical reaction potentials given, another change in rate of pressure drop is observed at twice the voltage of the first reaction noted.

Efficiency of electron activation. The main interest in the discussion of electron-activated reactions so far has been the determination of the minimum voltages through which electrons must fall in order to put neutral normal molecules into a reactive state. In every case the new species of molecule or ion was determined from the known energy states as obtained from spectroscopy or the mass-spectrum analysis. Another question of great interest is: How many electrons or ions or excited molecules are necessary to produce a molecule of the product or are needed to remove a molecule of the reactant? The efficiency of the reaction can be stated in a variety of ways, and this quantity should permit further insight into its mechanism. Several investigators have determined the electron efficiency of the reaction studied by calculating the number of molecules either decomposed or formed and comparing this number with the number of electrons needed to remove or produce them.

The situation is as follows: Consider that M molecules of a gas disappear per second in an electron-activated reaction or that M molecules of the product are formed. It is clear that the same change may be considered from these two points of view. The number E of electrons which cross the reaction region per second can be calculated from the current. These electrons will make inelastic collisions leading to excitation or ionization with certain efficiencies (e) of resonance or ionization. If each electron in crossing makes Z collisions, the number of efficient collisions per second will be EZe. This number will represent the activated molecules produced per second in the impact space. In order that the reaction may be completed the activated species must impinge with other normal molecules and they must make collisions which will depend on their own concentration and on the concentration of the other molecules. Of this number (y) only a fraction (e') will lead to successful reaction. The total number of molecules which change per second will then be

$$M = EZeye'$$

They will depend on the type of activation, and at a given high velocity of electrons several modes of activation are possible so that

$$M = M_1 + M_2 + \cdots$$

such that for each group M_1, $M_2 \cdots$ the above consideration should be applied. For each of these groups the factors e, y, e' will be different, and the general relation is seen to be one of considerable complexity. At present, experiments on electron activation have to be carried out with electron streams of considerable velocity distribution, and most molecules have many and closely spaced energy states so that these studies can be made only within certain voltage ranges. However, at a given voltage a certain type of transition may well have high efficiencies (e and e') such that this mode of activation will predominate over other possibilities. For instance, after the ionization potential has been reached the excitations may be possible only with much smaller efficiencies, and then the ratio of molecules reacting per ion pair is of significance in the interpretation of the reaction. In this case

$$N = EZe$$

would indicate the number of ion pairs produced per second by E electrons crossing the tube, and

$$\frac{M}{EZe} = ye' = \frac{M}{N}$$

would be the M/N ratio which has been used to study radiochemical reactions. It is seen that this ratio can be considered as the product of two factors, one depending upon the number of impacts an ion makes and the other representing the chance that such an impact is an efficient one leading to reaction. At present many of the factors involved in this analysis of electron-activated changes are not known for most molecules, and these ideas can only be outlined as a guide for the further study in this field. However, in two of the investigations mentioned above, attempts of this kind have been made, Wansbrough-Jones (26) determined the number of molecules of nitrogen peroxide formed per ion pair to be 0.7. This value agrees with the radiochemical reaction studied by Lind and Bardwell (I,7), who obtained $M/N = 1$. Busse and Daniels (30) studied the same case with high-speed cathode rays and deduced $M/N = 0.5$. Glockler and Wilson (18) discussed these questions of efficiency of reaction and M/N ratio for the electron activation of oxygen.

It is clear that these changes produced by slow electrons of known speed are of the greatest importance in the study and elucidation of all electrical gas reactions. Through such investigations it will be possible to obtain further insight into the complexity of chemical changes occurring in discharge tubes, ozonizers and the electric arc. A start in the right direction has been made, but a great deal of work remains to be done. The whole problem needs the help of the physicist, who must determine the complete energy diagram of every molecule, and of the chemist, who must find out how the various energy rich species react with one another.

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CHAPTER VI

ATOMS AND RADICALS IN DISCHARGE TUBES

Spectroscopy of atoms and molecules. The luminous discharge is the most convenient device for the production of atoms and radicals in excited states and for the study of their spectra. It is evident that these energy-rich species must be considered as possible agents in the reactions which occur in the various forms of discharge discussed earlier (Chapter I). The spectra of compound molecules reveal at once that far-reaching dissociation has taken place. Any hydrocarbon molecule will show the CH-bands indicating that at least a detectable portion of them has been decomposed to yield a spectrum of the type mentioned. The carrier of this spectrum has been definitely identified to be a diatomic molecule of the proper moment of inertia and mass 13. Although there is no doubt that atoms and radicals of bewildering variety can be produced from a complex molecule under electrical excitation, one must guard against a too hasty conclusion in assuming that the complete mechanism of chemical reaction in electrical discharge follows necessarily only one path involving neutral atoms and radicals in either their normal or their excited states. There can be no doubt but that these structures are chemically active, for the whole science of photochemistry deals with reactions whose activation is accomplished by neutral energy-rich species. But in a discharge tube ions are also present, and they need to be considered in the whole complex situation. Again it must be said that the whole question is one of the relative importance of the various reactive types.

Innumerable researches have been carried out in the field of band spectroscopy, and a much larger number of studies will have to be made before all the diatomic molecules conceivably formed from ninety-two elements are known in relation to their various energy states. If polyatomic molecules are next considered it is seen that their spectroscopic behavior has been studied hardly at all. Their spectra will more likely be found to be continuous. During the usual spectrographic study no attention is paid to the possible chemical reactions which occur in the discharge, although their existence may be recognized. It is, of course, impossible even to summarize the situation pertaining to the purely spectroscopic studies. Both methine (CH) and imine (NH) have been observed spectroscopically and postulated as reactants in many mechanisms as mentioned by Willey (146). They have not been studied as much as the hydroxyl radical and the behavior of atomic hydrogen, oxygen and nitrogen. This radical and these atoms have been considered in various mechanisms of thermal, photochemical (113) and sensitized reactions and in dilute flames. A review of atomic reactions has been given by Geib (165). We will consider only such researches where the atomic or radical species have been produced in electrical discharge.

Free radicals. The spectrum lines of free diatomic radicals are the most direct evidence for their existence. The important role they play in the progress of chemical reactions is in many cases merely a matter of surmise. To be sure, frequently no other than some sort of radical mechanism seems to offer a sensible picture of the progress of a reaction. Thermal, photochemical and sensitized photochemical reactions may differ in their mode of initiation or activation, but in many instances radicals or atoms are involved in the reaction sequence. Even though no direct proof exists for the participation of radicals and atoms, the circumstantial evidence in certain instances is so strong that one readily accepts the picture proposed. Such is the case with the free aliphatic radicals discovered by Paneth (61) and his co-workers and studied in detail by Rice (157). These radicals can be produced by the pyrolysis of organic compounds or by electric discharge. Many vapors after such treatment will interact with lead or antimony mirrors, as the products of decomposition are drawn over these metal deposits in the flowing gas. Neither zinc nor cadmium mirrors are affected, and the interactions do not seem to be due to atomic hydrogen (vide infra). Rice (157, page 43) mentions an interesting observation: "Even on heating to 1000° ethylene does not remove mirrors; however when passed through a discharge tube it removes antimony readily and lead mirrors more slowly." It appears that a reactive state is produced by the electric discharge which cannot be duplicated readily by other means. We must then consider the possibility of a free radical mechanism of reaction in electric discharge, but also recognize that the action of the discharge differs from other modes of activation.

Atomic species. The spectra of discharges show atomic lines indicating the presence of atoms. Most of the elements have been studied in this respect, and the science of atomic spectroscopy has been the foundation of our modern concepts regarding the constitution of matter. In several instances it has been possible to remove the atoms of an otherwise diatomic gas from the producing discharge; hydrogen, oxygen, nitrogen and halogen atoms have been obtained in flow systems downstream from the electrical discharge. These atomic species show very different chemical behavior from their diatomic parents. Since the presence of atoms in discharge tubes is shown by their spectra, they must be considered as possible agents for the initiation and propagation of chemical reactions.

Spectra and reactions of organic compounds. It is of interest to cite an example of a study in glow and electrodeless discharge where both the chemical transformations and the spectra were investigated. Such a case is furnished by the work of Harkins and co-workers (73, 119, 135) with certain organic substances. The chemical effects have already been mentioned (Chapter III), and it remains to show that during these reactions radiations are emitted which reveal the presence of atoms and radicals. The fragments found and recognized by their spectra were: CH, OH, NH, C_2, CN, N_2, CO, CO^+, CS, S_2, H_2, C, C^+, H, S, H_2O and NH_3. These radicals and atoms were present when such substances as benzene, xylene, mesitylene, methane, pyridine, benzaldehyde, thiophene, *n*-heptane, phenol and others were treated in the discharge. The spectra produced by a given substance, for example benzene, show some differences in the various forms of discharge. As compared with the electrodeless discharge in benzene, the spectrum of the glow discharge differs in the following respects: Only the fourth group of the Swan bands appears to any extent, i.e., the C_2 bands are much less developed. The atomic or line spectrum of carbon is not so intense, and the prominent line 4367 Å of ionized carbon is not found. The CH bands are very clear, and the 3900 Å band is closer in intensity to the 4300 Å band than in the electrodeless discharge. The hydrogen Balmer lines are slightly more intense, and the many-line spectrum of molecular hydrogen, not present in electrodeless discharge, is prominent. Harkins and Jackson (119) find that the greatest intensity of the spectrum is given by the cathode glow and the edge of the negative glow nearest to the cathode. One would then deduce that the maximum reaction should take place in these regions if these radicals are involved in the chemical reaction. However, we need to recall that the greatest concentration of ions also is found in these most luminous portions of the discharge. Hence no decision can be made regarding an ionic or atomic or radical mechanism of reaction. We must also remember that the concentration of a given radical need not be great to be revealed by spectrographic means and it is conceivable that the main reaction may go by a path not involving the groups found by the radiations they emit. It is seen that the usual carriers of the known hydrocarbon spectra are all formed in the discharge tubes. Whenever another element such as sulphur or nitrogen is present in a substance, the spectrum of some radical containing these elements is found. Atomic hydrogen is observed in all cases. One is impressed by the fact that most diatomic radicals whose spectra are known and which can conceivably be produced will appear. The further remarkable fact should be recalled (Chapter III) that with many substances, as for example benzene, large amounts of solid reaction product can be obtained without any accumulation of gaseous materials. In other words, the various radicals and atoms must all combine neatly into the solid polymer! At least, such would have to be the conclusion in case one adopts a reaction mechanism involving radicals and atoms only. An observation of interest in this connection was made by Bonhoeffer and Harteck (38) on acetylene entering a stream of active hydrogen (atoms) in a flow system at low pressure. A beautiful, intense light was emitted from the gas stream, but only very small amounts of the reaction product could be frozen out. Most of the acetylene comes through the ordeal unscathed. In other words, a great deal of radiation may be given out from a potentially reactive system and no reaction may happen. The process

$$H + C_2H_2 \rightarrow \text{Products}$$

is unlikely, whereas

$$H + H + C_2H_2 \rightarrow CH^* + CH + H_2 \rightarrow C_2H_2 + H_2 + h\nu$$

occur frequently. It is possible to have free radicals and atoms present in a reaction system and no change result. Light emission and chemical reaction are not necessarily concomitant phenomena.

Atomic hydrogen. Of the many gaseous substances which have been investigated in electric discharges and for which a great deal of evidence as to their existence in the atomic state has been accumulated, hydrogen must take first place. Langmuir (2, 3, 4) showed very early that hydrogen molecules will dissociate into atoms when allowed to impinge on very hot metal wires. He studied the chemical phenomena involved at low pressures and established the fact that hydrogen atoms could be frozen out at glass surfaces when cooled to liquid-air temperatures.

Triatomic hydrogen. Although these experiments established the nature of active hydrogen as an atomic modification of the element, it may be mentioned that other attempts to find a triatomic form have been unsuccessful. Thomson (1) found the triatomic hydrogen ion (H_3^+), but the neutral structure seems to be quite unstable. Many investigators (5, 6, 8, 9, 10, 12, 13, 16, 17, 18, 20, 26, 28, 32, 33, 36, 37, 41, 43, 47, 48, 49, 62, 80, 84, 92, 96, 99, 118, 129, 145, 150) have studied this problem, but the evidence for the existence of triatomic hydrogen is not as satisfactory as that for the monatomic form. From theoretical considerations Eyring and Polanyi (89) and Eyring (102) ascribe to H_3 a slight stability.

Wood's hydrogen. Wood (7) wanted to obtain the higher members of the Balmer series of atomic hydrogen, and to this end he studied the spectra obtained in very long discharge tubes. He investigated the behavior of these long tubes under a variety of conditions and found a most extraordinary situation. The center region of such a long tube could be observed end-on by appropriate bending and construction. At one stage the Balmer lines could be seen with great brilliancy, and under different conditions the secondary spectrum would be very prominent. In the second stage the color of the discharge was white, and in the first stage it was reddish, owing mainly to the hydrogen alpha line. The secondary spectrum was then reduced to a very low intensity. Wood discovered that moist hydrogen gas gave the Balmer spectrum strongly and that dry hydrogen gas produced the secondary spectrum. He could put a discharge tube into the desired condition at will by simply allowing the hydrogen gas entering the tube to pick up a little moisture or by drying it carefully. The whole complex of observations finds its ready explanation in the assumption that hydrogen atoms are produced in the discharge in abundance and that they live long enough to be drawn out of the discharge proper and recombine further downstream in the side tube. At the pressures generally used (1 mm. or less), recombination of atoms in the gas phase takes place infrequently because triple collisions are rare. Reunion of atoms must occur mostly on the walls of the reaction vessel.

The catalytic effect of the wall. Langmuir (2) suggested that the added water vapor decomposed in the discharge, furnishing a little oxygen which is adsorbed on the inner glass walls and poisons the glass surface which when clean serves as a catalyst for the recombination of the hydrogen atoms produced in the discharge. With dry hydrogen the secondary spectrum due to molecular hydrogen is prominent because the atoms are then recombining on the wall at such a rapid rate that their concentration never reaches a sufficiently high value to produce the Balmer spectrum with any intensity. On the other hand, with the catalytic walls poisoned, the hydrogen atoms accumulate, because they can only recombine in the gas phase by means of triple collisions which are rare occurrences at the low pressures used. Later investigators found other substances besides water vapor and oxygen which would poison the wall. Hansen (21) found ice to be a negative metals behave similarly. Several substances such as anthracene will fluoresce and zinc sulphide will phosphoresce in atomic hydrogen. The most interesting observation made by Bonhoeffer is the finding that the resonance line of mercury ($\lambda = 2537$ Å) can be excited by atomic hydrogen. But the energy of this radiation is 4.9 e.v., which is greater than the available energy, supposing that active hydrogen is atomic in form! However, $\lambda = 2537$ Å is always accompanied by certain mercury hydride bands. It seems that the simple process:

$$2H + Hg \rightarrow H_2 + Hg^*; \quad Hg^* \rightarrow Hg + h\nu \text{ (2537 Å)}$$

must be replaced by a more complicated one

$$Hg + H \rightarrow HgH; \; H + HgH \rightarrow Hg^* + H_2; \; Hg^* \rightarrow Hg + h\nu\text{(2537 Å)}.$$

These reactions are the reverse ones pertaining to the famous Cario and Franck (11) experiment, and the second set of steps has been discussed by Compton and Turner (15). Hydrocarbon gases reacting with atomic hydrogen show the CH and C_2 bands (38). Acetaldehyde chemiluminesces in the region 4000–4260 Å (66).

Reactions of atomic hydrogen with hydrocarbons. Atomic hydrogen reacts readily with hydrocarbon gases except methane. Bonhoeffer and Harteck (38) studied methane, ethane, pentane, petroleum ether, ethylene, acetylene and benzene. The main reactions are hydrogenation, dehydrogenation and ring rupture. The dehydrogenations follow the reaction scheme

$$C_nH_m + H \rightarrow C_nH_{m-1} + H_2$$

except methane which does not react at room temperature by exchange of the type

$$CH_4 + H \rightarrow CH_3 + H_2; \; CH_3 + H \rightarrow CH_4$$

as can be deduced from the fact that the glass walls of the reaction tube never became warm.

The hydrogenations seem to take place on the wall, as the most likely gas phase mechanism

$$C_2H_4 + H \rightarrow C_2H_5; \; C_2H_5 + H \rightarrow C_2H_6$$

would involve association reactions which are not supposed to occur in bimolecular collisions. The cracking action of hydrogen atoms may be

$$C_2H_6 + H \rightarrow CH_3 + CH_4$$

All these changes were observed in the stream of gas coming from the discharge tube where the atomic hydrogen was produced. Although in these particular experiments the hydrocarbons were added "downstream" it is clear that these reactions must also occur in the discharge itself if the hydrocarbons are introduced therein. However, other than atomic and radical mechanisms cannot be denied as possible in the discharges. It must be remembered, for example, that methane reacts as readily in electric discharge as do other hydrocarbons.

Reactions at low temperatures. At ordinary temperature, hydrogen atoms do not undergo addition reactions, because at higher temperatures the products formed may readily be decomposed again since the needed heat of activation can be supplied. For example,

$$Hg + H + (M) \rightarrow HgH + (M); \; HgH + H \rightarrow Hg + H_2$$

may happen at high enough temperature, while at liquid-air temperature, the second reaction, requiring an activation energy, may be repressed and the resulting mercury hydride will be stable. In this manner addition products of hydrogen and nitric oxide: $(HNO)_x$, of hydrocyanic acid: (H_3CN) and cyanogen and sulphur dioxide have been prepared by Harteck (120) and by Geib and Harteck (134). Acetylene, ammonia, methyl amine and nitrous oxide gave no signs of combining with active hydrogen at low temperature.

General reactions of atomic hydrogen. The reactions of hydrogen atoms are given below. In many cases the products have not been studied in sufficient detail to warrant writing equations. However, the results of these changes are in general what one might expect from the reduction of the reactant in question. The atoms are produced in a glow discharge in a flow system, but the reactions take place downstream. (Substances not reduced by *H* are so designated.)

Inorganic substances: Ag, AgF, AgCl, AgBr, AgI, Ag_2O, $AgNO_3$; As; Au; Ba; Bi, Bi_2O_3, $BiCl_3$, $Bi(NO_3)_3$; $Ba(NO_3)_2$; $Ca(NO_3)_2$; Cd, CdO, CdS, $CdCl_2$, CdI_2, $CdCO_3$, $Cd(NO_3)_2 \cdot 4H_2O$, $CdSO_4 \cdot \frac{8}{3}H_2O$; $CoCl_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Co(NO_2)_6K_3$; $CrCl_3$, $CrCl_3 \cdot 6H_2O$, Cr_2O_3; Cu, Cu_2O, CuO, CuS, Cu_2S, CuCl, CuF, CuF_2, $CuSO_4 \cdot 5H_2O$; Fe_2O_3, $FeCl_2$, $FeCl_3$, $FeSO_4$, $Fe(CN)_6K_4$, $Fe(CN)_6K_3$; Ga; Ge; Hg, Hg_2O, HgO, HgS, HgCl, $HgCl_2$, $HgSO_4$, Hg_2SO_4; HIO_3 (starch); In; K, KCN, KCNS, $KClO_3$, $KClO_4$, KNO_2, KNO_3; Li, $LiNO_3 \cdot 3H_2O$; MnO_3, MnO_2, $MnCl_2$; NH_4NO_3; Na, $NaBrO_3$, NaN_3, $NaNO_2$, $NaNH_2$, Na_2S, Na_2SO_3, $Na_2S_2O_3$, Na_2SeO_3; $NiCl_2 \cdot 6H_2O$, $Ni(NO_3)_3 \cdot 6H_2O$, NiO; P(red), P_2O_5, H_3PO_4 (cryst.); Pb, PbO, Pb_3O_4, PbO_2, $PbCl_2$, $PbSO_4$, $PbCrO_4$, $Pb(CH_3COO)_2 \cdot 3H_2O$; $PtCl_6Na_2$; S; Sb, Sb_2O_3;

silico molybdic acid; Sn, SnO_2, $SnCl_2 \cdot 4H_2O$. (Refs. 14, 20, 66, 70, 79, 104, 117, 122, 123, 132, 134, 139, 148, 163, 167.)

Inorganic substances (not reduced by H): $AlCl_3$; $CaCl_2$, CaF_2, CaC_2; $CdCl_2 \cdot 4H_2O$ (moist); $Cr_2(SO_4)_3$; KI, KCl, KNO_3; MgO, $MgCl_2$; $NaNO_3$, $(NH_4)_2SO_4$; $(SbOKC_4H_4O_6) \cdot \frac{1}{2}H_2O$; $ZnCl_2$, ZnO. (Refs. 14, 167.)

Solutions of inorganic substances: Ag^+; Ca^{++}, Cu^{++}; $Cr_2O_7^{--}$; H_2O_2; HI, I_2; $Se_2O_3^{--}$; Hg^{++}, Hg^+; MnO_4^-; SO_3^{--}. (Refs. 105, 167.)

Organic substances: Oleic acid → stearic acid; indigo carmine, indigotin II, orange II, safranine T, azobenzene → hydrazobenzene → aniline, pontamine diazo black, auramine O, Indigo, $3CH_3COH \rightarrow (CH_3COH)_3$, olive oil, metacresol, chinoline, nitrobenzene, cinamic aldehyde, cinamic acid ethyl ester; indigo sulphuric acid, methylene blue; Schuman plate. (Refs. 14, 20, 57, 60, 66, 107, 108, 112, 153, 167.)

Organic substances (not reduced by H): Leucomethylene blue (solution); benzoic acid; acetamide; $-COOH$. (Refs. 66, 167.)

Organic vapors: $H + H + (HCOOH) \rightarrow H_2 + (HCOOH)$; $HCOOH \rightarrow CO + H_2O + H \rightarrow HCOH + H \rightarrow CO + H_2$. $C_6H_6 + H \rightarrow CH_4(20\%)$, $C_2H_2(5\%)$, C_2H_4, C_2H_6; $CH_3X + H \rightarrow HX + CH_4$ or C_2H_6 or C_2H_4 (X = Cl, Br, I, OH); $C_2H_5X + H \rightarrow HX + H.C. + X_2$ (X = Cl, Br); from CH_3F (no reaction) to CH_3I (100%); CH_2Cl_2, $CHCl_3$, CCl_4, CH_3Br, CH_3I, C_2H_5I; C_5H_{12}; $HCCl_3$. (Refs. 14, 66, 114–117, 128, 134, 167.)

Hydrocarbon gases: $CH_4 + H \rightarrow$ no reaction; $C_2H_6 + H \rightarrow CH_4$ (25%), C_2H_2, C_2H_4; $C_nH_m + H \rightarrow C_nH_{m-1} + H_2$; $C_2H_4 + 2H \rightarrow C_2H_6$ (50%), C_2H_4; $C_2H_2 + H \rightarrow$ addition product (at −190° C.) (2 to 3% react at room temperature; may be due to oxygen). (Refs. 14, 38, 67, 114.)

Gases which do not react with H: C_2H_2 (luminescence but no reaction); CH_4 (no reaction, no exchange at room temperature); CO (trace of HCOH); CO_2 (trace of HCOH); N_2; NH_3; CH_3NH_2. (Refs. 14, 25, 82, 100, 117, 134.)

Sulphur compounds: $H + SO_2 \rightarrow$ Products. (Refs. 117, 134.)

Mixtures of gases: $CO + N + H \rightarrow CO(NH_2)_2$; $(H) + H_2 + \frac{1}{2}O_2 \rightarrow H_2O + (H)$; $H + O_2 + H_2 \rightarrow HO_2 + H_2$ or $O_2 \rightarrow H_2O + OH$; $HO_2 + H + \text{Wall} \rightarrow H_2O_2$ (below −80° C.); $CO + O_2 + H \rightarrow CO_2 + OH \leftarrow HO_2 + CO$; $CO + O_2 + H \rightarrow H_2O_2 + H_2O + CO_2$ (−190° C.); $CO + O_2 + H \rightarrow H_2O + CO_2$ (high temperature); $CH_4 + O_2 + H \rightarrow H_2O + CO_2$ (25° C; 100° C) (no reaction −190° C.); (H or $O + CH_4 \rightarrow$ no reaction!!); $C_2H_2 + O_2 + H \rightarrow H_2O + CO_2 + C_2H_2$; C_6H_6 +

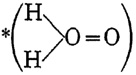
$O_2 + H \rightarrow H_2O + CO_2 + C_2H_2 + C_6H_6$; H_2O (discharge) $\rightarrow H + OH +$ etc.; $H + OH +$ etc. $\rightarrow HO_2$ (intermediary); $HO_2 +$ etc. $+ CO \rightarrow CO_2 +$ etc. (Refs. 42, 54, 71, 134, 152.)

Recombination of H: $H + H + M \rightarrow H_2 + M$ (M = wall or gas), effective gases: $M = HCl, HBr, H_2S, CH_3Cl, C_2H_2, C_2H_6$, (in the case of HCl: $H + HCl \rightarrow H_2 + Cl$ and $Cl + H +$ Wall $\rightarrow HCl$); ineffective gases: N_2, H_2O, NH_3, CH_4. (Refs. 25, 67, 158.)

Halogens reactive with H: $H + Cl_2 \rightarrow HCl + Cl$; $H + Br_2 \rightarrow HBr + Br \rightarrow HBr$. (Ref. 25).

Gaseous nitrogen compounds: $H + N + (M) \rightarrow NH + (M) + H_2 \rightarrow NH_3$; $H_2 + N + (M) \rightarrow NH_2 + (M) \rightarrow N_2H_4$; $3H + N + (M) \rightarrow NH_3 + (M)$ (M = Cu, Zn, Fe, surface); $H + N + (M) \rightarrow N_2H_4 + (M)$ (M = Cu, Fe, Zn inefficient); $H + N_2H_4 \rightarrow NH_3 +$ etc.; $H + N \rightarrow NH_3$; $H + NO \rightarrow (HNO)_x$ (at liquid-air temperature; decomposes when heated above −90° C.); $H + HCN \rightarrow H_3CN$ (at liquid-air temperature; decomposes above −60° C.); $H + (CN)_2 \rightarrow$ products; $H + NH_3 \rightarrow$ no action; $H + N_2O \rightarrow$ no action; $H + N_2O \rightarrow N_2 + OH$ (activation >10 k-cal.); $N_2 + OH \rightarrow H_2O +$ etc.; $H + NO_2 \rightarrow NO + OH$. (Refs. 82, 88, 100, 101, 117, 120, 130, 134, 165.)

Oxygen and oxygen compounds: $2H + O_2 \rightarrow H_2O_2$; $2H + O_2 \rightarrow$ H_2O_2*



$\left(\begin{matrix} H \\ H \end{matrix}\!\!>O=O\right)$

(− 190° C., wall) $\rightarrow H_2O_2$ (on warming); $H + O_2 \rightarrow HO_2$ (intermediary); $2H + O_2 \rightarrow H_2O_2$ (below −80° C.) (wall); $2H + O_2 \rightarrow H_2 + O_2$; $H + O_2 \rightarrow OH + O$ (doubtful); $H + O_2 \rightarrow HO_2$ (probable in triple collision); $H + O_2 \rightarrow H_2O_2$ (liquid-air temperature); $H + H_2O_2 \rightarrow H_2O + OH$; $H + O_3 \rightarrow OH + O_2$. (Refs. 25, 104, 133, 134, 165, 171.)

Exchange reactions (Activation energy or heat of reaction (*) in kilo-calories given): $H + H_2$ (para) $\rightarrow H + H_2$ (normal); $H + D_2O \rightarrow H + HDO$ (12 ± 1); $D + H_2O \rightarrow H + HDO$ (12 ± 1); $D + NH_3 \rightarrow H + NDH_2$ (11 ± 1); $D + C_2H_2 \rightarrow H + C_2HD$ (<5); $D + CH_4 \rightarrow$ no exchange (>11); $D + CH_4 \rightarrow CH_3 + HD$ (11.7); $D + C_2H_6 \rightarrow C_2H_5 + HD$ (6.3); $D + CH_4 \rightarrow CH_3D + H$ (15.6); $D_2 + CH_3 \rightarrow CH_xD_y + D$ (11.1); $D + CH_4 \rightarrow CH_3 + HD$ (−4.5*); $HD \rightarrow H + D$ (−103.5*); $CH_4 \rightarrow CH_3 + H$ (−108.0*); $D + C_2H_6 \rightarrow CH_3 + CH_3D$ (7.2); $D + C_2H_6 \rightarrow C_2H_xD_y + H$ (11.4); $D + C_3H_8 \rightarrow C_2H_xD_y +$ etc.; $D + C_4H_{10} \rightarrow C_2H_xD_y +$ etc.; $2CH_3 \rightarrow C_2H_6$ (−97.6*). (Refs. 90, 149, 169, 170.)

From a study of this material it is seen that most compounds are attacked by atomic hydrogen, although some are stable towards this powerful reducing agent. As Kroepelin and Vogel (167) point out, it is necessary that the active gas penetrate into the solid. Furthermore the hydrogen atoms must be able to diffuse through the reaction product formed on the surface. Clearly the initial reactants and the products must not be too good catalysts for the recombination of hydrogen atoms. The heavy metal salts are easily reduced, as would be expected from their usual chemical behavior. The anion has an influence on the general reducibility of a salt. Alkali salts can be reduced to the metal if the anion is of such a nature that it is destroyed by active hydrogen (NO_3^-, NO_2^-, CN^-). The nitrates of the alkaline earths can be decomposed only to the oxides. Dyes can be converted to their leuco forms readily, but the carboxyl group ($\cdot COOH$) is not affected. Many materials will aid the recombination of hydrogen atoms and hence serve as catalysts without themselves suffering reduction. The reducibility may vary greatly within a series of related compounds. Methyl fluoride shows no action, but methyl chloride interacts quantitatively with atomic hydrogen.

Induced oxidations. Although hydrocarbons will not react with molecular oxygen at ordinary temperature, they will do so in the presence of atomic hydrogen, as Geib and Harteck (134) have shown (mixtures of gases). Many studies between hydrogen and oxygen lead to the view that an important reaction complex is the radical HO_2:

$$H + O_2 + (M) \rightarrow HO_2 + (M)$$

which is discussed, for example, by Rodebush (171).

Exchange reactions. All sorts of interesting exchange reactions are possible, especially when deuterium atoms are involved, for then it is possible to learn about the progress and extent of exchange because the thermal conductivity of the gaseous reaction mixture can be determined. Important information regarding activation energies for such exchange reactions can be obtained by varying the temperature. It is seen that the exchange of deuterium and methane requires a large heat of activation. This reaction, therefore, will not take place at ordinary temperatures.

Solution reactions. Harteck and Roeder (166) added neon gas to the discharge to a total pressure of 20 mm. Hg with a few tenths of a millimeter of hydrogen, oxygen or nitrogen. In such a system it is possible to study water solutions which have a vapor pressure of about 4 mm. and hence would boil if hydrogen only were used. The usual luminous discharge will not operate satisfactorily at pressures of hydrogen sufficiently high to prevent rapid evaporation of water solutions. The rare gases, however, will carry a glow discharge readily at higher pressures. Several oxidation and reduction reactions were investigated by means of atomic species. These were drawn from the gas discharge in the usual manner and passed in a flow system through various solutions.

Direct evidence for atoms. In the case of hydrogen, oxygen and nitrogen Wrede (50, 68) and Harteck (55) obtained very direct indications of the presence of atoms in electric discharges. If two vessels are connected by a small aperture and if in one of the spheres the gases are dissociated under the influence of the glow discharge and in the second volume recombination only happens, then a difference in pressure will be developed which gives a measure of the concentration of the atoms. Spark discharges lead to a greater concentration of atoms, as might be expected. The volume percentage (n) of atoms is given by (165)

$$n = \qquad \begin{array}{r} - p_2) \\ - 0.5\sqrt{2}) \end{array}$$

where p_1 = pressure in bulb containing atoms and molecules; p_2 = pressure in bulb containing molecules only.

Recombination of atomic hydrogen. The spectroscopic and chemical evidence for the atomic constitution of hydrogen activated in electrical discharge and drawn from the place of production seems as direct as can be expected. A special study by Bay and Steiner (52) of the gases nitrogen, oxygen and hydrogen showed that the disappearance of the molecular hydrogen spectrum and the simultaneous appearance of the Balmer series are proportional to the hydrogen concentration as determined by the method of Wrede (50, 68). A number of investigators (23, 52, 63, 64, 67, 75, 81, 97, 98, 105, 110, 111, 124, 140, 142, 143, 147, 161) have studied the recombination of atomic hydrogen and found it to be a trimolecular process

$$H + H + (M) \rightarrow H_2 + (M), \; (M = H, H_2, A, N_2, \cdots)$$

as is to be expected on our modern views of recombination reactions in the gas phase. The efficiency in triple collision of hydrogen atoms is not as great as of hydrogen molecules (131). On the wall we must expect

$$H + W \rightleftarrows HW; \quad H + HW \rightleftarrows H_2 + W \; (W = \text{Wall})$$

Hydrogen arc welding. Atomic hydrogen produced in an electric arc has been adapted for welding purposes by Langmuir (22, 27, 29, 46), and others (51, 87, 121) have discussed this industrial use. The large heat of recombination (102.7 k-cal. per mole) is released at the metal surface which acts catalytically, raising the temperature to a high value. The reducing atmosphere of the hydrogen is a further advantage in this type of welding.

Atomic oxygen. The method of Wood was used by several investigators for the production of atomic oxygen from the moist gas. Bichowsky and Copeland (30) and Copeland (40, 53) reported an active form of the gas which exhibited a pressure effect near an orifice and which heated a nearby platinum strip. Evidently oxygen atoms present in the gas and drawn from the discharge through a side tube would produce these effects as do hydrogen atoms. Copeland (69) and Rodebush and Troxel (78) obtained about 20% dissociation into atoms. The heat of dissociation was found to be 131 k-cal. Herzberg (76) reports 117 k-cal. from spectroscopic information. Several investigators determined the chemical properties of atomic oxygen. Glass walls act as catalysts for the recombination of oxygen atoms. Mercury vapor is readily oxidized to yellow mercuric oxide by atomic oxygen. Traces of nitrogen form compounds and produce an afterglow. Small specks glow white hot as in atomic hydrogen. Palladium, platinum and nickel are good catalysts for recombination; copper and tungsten are not effective.

Direct evidence for the existence of atoms was also obtained by Wrede (68) and by Bay and Steiner (52). The latter found increased intensity for certain arc lines of atomic oxygen in the effluent gas from a Wood's tube by applying an auxiliary discharge. The former noted pressure differences on two sides of a narrow slit, showing atoms to be present.

Reactions of atomic oxygen. The atoms of oxygen are produced in the glow discharge, but the chemical reactions mentioned below take place down stream in a flow system.

Inorganic substances: $Hg + O \rightarrow HgO$; $PbO + O \rightarrow PbO_2$. (Refs. 58, 69.)

Inorganic substances in solution: $FeSO_4 + O \rightarrow Fe^{+++} + \text{etc.}$; $KI + O \rightarrow I_2 + \text{etc}$; $KBr + O \rightarrow KBrO_3, Br_2 + \text{etc.}$; $NaCl + O \rightarrow NaClO_3$; $NH_4Cl + O \rightarrow NH_4ClO_3$; $Na_2C_2O_4 + O \rightarrow CO_2 + \text{etc.}$; $(N_2H_4 \cdot H_2)SO_4 + O \rightarrow$ products. (Ref. 166.)

Inorganic gaseous substances: $H_2 + O \rightarrow OH + H \rightarrow H_2O$ (0 to 2% conversion; afterglow decreases); $H_2 + O \rightarrow$ no action (at −183° C.); $H_2 + O \rightarrow OH + H$ (no action at low pressure); $H_2O_2 + O \rightarrow OH + HO_2 \rightarrow H_2O, H_2, H_2O_2$ (0 to 2% conversion); $HCl + O \rightarrow H_2O, Cl_2, Cl_2O$ (5%), (10 to 25% conversion); $HCl + O \rightarrow H_2O, Cl_2, Cl_2O$ (50% react at −183° C.); $HBr + O \rightarrow H_2O, Br_2$, (100% conversion).

(Refs. 56, 73, 91, 117, 134, 165, 171.) $NH_3 + O \rightarrow HNO$ (?) or $(NH_4)_2N_2O_2$ (explosive product) (10 to 25% conversion); $NH_3 + O \rightarrow$ products (50% react at −183° C.); $H_2S + O \rightarrow H_2O, SO_2, SO_3, H_2SO_4$, etc. (100% conversion); $NO + O \rightarrow NO_2$ (triple collisions, oxygen afterglow); $NO + O \rightarrow NO_2$ (10% react at −183° C.); $N_2O + O \rightarrow$ no action (at −183° C.); $NO_2 + O \rightarrow NO + O_2$ (at every 10^5 collision); $xN + yO \rightarrow N_xO_y$; $O_2 + O \rightarrow O_3$ (at liquid-air temperature); $SO_2 + O \rightarrow SO_3$ (8% react at −183° C.); $Xe + O \rightarrow$ no action. (Refs. 69, 74, 91, 117, 134, 160.)

Organic gaseous substances: $HCN + O \rightarrow H_2O, (CN)_2, CO_2, NO$ (2% to 5% conversion); $HCN + O \rightarrow H_2O, (CN)_2, CO_2, NO$ (no reaction at −183° C.); $CH_4 + O \rightarrow CO_2, H_2O, CO$ (0 to 2% conversion); $CO + O \rightarrow CO_2$ (2 to 5% conversion); $CO + O \rightarrow CO_2$ (1.3% react at −183° C.); $HCOH + O \rightarrow OH + COH \rightarrow H_2O_2, CO_2$ (25%), CO (40%), H_2 (40%); $HCOOH + O_2 \rightarrow CO_2$ (90%), CO (small), H_2O; H_2O + discharge $\rightarrow OH + H$; $OH + CO \rightarrow CO_2 + H$ (up to 30% react); $CCl_4 + O \rightarrow COCl_2, Cl_2$, (1:1) (2 to 5% conversion); $(CN)_2 + O \rightarrow CO_2, H_2O, N_xO_y$ (2 to 5% conversion); $CHCl_3 + O \rightarrow COCl_2$, HCl (100% conversion); $CH_3Cl + O \rightarrow HCl, Cl_2, H_2O, CO_2, CO$; $CH_2Cl_2 + O \rightarrow COCl_2, H_2$, ($Cl_2$, HCl, H_2O, CO_2, CO as secondary products) (100% conversion); $CH_3OH + O \rightarrow CO_2, CO, H_2O, H_2$ (100% conversion); $CS_2 + O \rightarrow SO_2, CO, CO_2$ (100% conversion); $CH_3NH_2 + O \rightarrow NH_3, NO, CO, C_2H_4, CH_4, H_2$ (50% conversion at −183° C.); $C_2H_2 + O \rightarrow CO_2, H_2O$, etc. (100% conversion); $C_2H_2 + O \rightarrow$ addition product (at −183° C.) and the addition product $\rightarrow$ CO, $(HCO)_2$, HCOOH, CO_2, H_2O on warming (67% conversion at −180° C.); $C_2H_4 + O \rightarrow CO, HCOOH, CH_3COH$ (67% conversion at −183° C.); $C_2H_6 + O \rightarrow CO_2$, etc. (2 to 5% conversion); $C_2H_5OH + O \rightarrow CO_2$, etc. (100% conversion); $(CH_3)_3N + O \rightarrow$ (HCOH), CO, C_2H_4, CH_4, H_2 (50% conversion at −183° C.); $C_5H_{12} + O \rightarrow CO_2$, etc. (10 to 25% conversion); $C_6H_6 + O \rightarrow C_6H_6O_{3.15} \cdot 1.08H_2O$ (10% conversion at −183° C.); $C_6H_6 + O \rightarrow$ addition product (100% conversion at −80° C.); addition product $\rightarrow CO_2$ (2%), CO (1%), HCOOH (10%), H_2O (on warming to −30° C.) and $C_6H_6O_{3.55} \cdot 0.26H_2O$; $C_6H_6 + O \rightarrow$ products (100% conversion); $C_6H_6 + O \rightarrow C_6H_5OH$, etc.; $C_6H_{14} + O \rightarrow CO_2$, etc. (10 to 25% conversion). (Refs. 74, 91, 94, 117, 134, 165.)

Many times these transformations were accompanied by chemiluminescence. For example, hydrocarbons showed the CH and C_2 bands. OH bands were also found. The relative intensity of the CH:OH bands decreased from benzene over ethylene to the saturates. The formation of ozone was shown to be negligible (136) except at low the OH spectrum depend on a wall reaction, as was shown to be the case.

They believe the reactions

$$H + H + (M) \rightarrow H_2 + (M);\ OH^* \rightarrow OH + h\nu$$

$$OH + OH \rightarrow H_2O + O;\ O + O + (M) \rightarrow O_2 + (M)$$

represent the situation. But little evidence is at hand for the existence of oxygen atoms. The life of hydroxyl is estimated to be 0.001 sec. Dixon and Steiner (101) were unable to find the radical outside the discharge, and Stoddart (144) claims that hydroxyl cannot be removed from the generating region. However, when an afterglow is produced in moist oxygen, hydroxyl emission can be detected up to distances of a meter and a half from the exit end of the discharge tube. He thinks that in the experiments of Lavin and Stewart (59) a trace of oxygen in their water accounted for their ability to obtain the hydroxyl band, or a stray discharge reaching into the observation tube may have been responsible. Elimination of both factors made a repetition of their experiments impossible. The oxygen afterglow is accompanied by the water band, and he thinks that oxygen atoms are responsible for the production and excitation of hydroxyl. The chemical actions of hydroxyl are really caused by hydrogen and oxygen atoms always present on the Bonhoeffer-Pearson mechanism.

Chemical actions of hydroxyl. The active gas from a water discharge has both reducing and oxidizing properties (59) as shown by the reduction of copper sulphate and the oxidation of metallic silver. Urey and Lavin (66) found that water vapor from an electrical discharge is more active than similarly treated hydrogen, and they ascribe the enhanced activity to the presence of hydroxyl in the first case. Iron and nickel chloride are thus reduced by activated water vapor but not by hydrogen. However, others (167) appear to have been able to cause these reductions with active hydrogen. The condition of the surface of the reactants is of great importance in such experiments and may easily vary from one case to another, thus accounting for differences in observation. The conversion of indigo to the leuco compound was also much accelerated, and ethylene formed acetaldehyde.

The production of hydrogen peroxide in electrical discharge has been shown by several investigators (Chapter IX), and it has been considered that the combination of hydroxyls leads to its formation. High yields of hydrogen peroxide were obtained by Rodebush and Wahl (126) in a liquid-air trap located between the water-vapor discharge and the pumps. The yield was independent of the distance: discharge-trap. Silver and copper chromite destroyed the active agent and/or the hydrogen peroxide. The latter could not be found in the region where it was thought to have been formed, i.e., between the discharge and the trap. Nor could they observe either oxygen atoms or molecules by a molecular-ray experiment. After discussing the possible interaction of all conceivable species present, they decided that

$$OH + OH \rightarrow H_2O_2$$

represented the actions in the gas. Since such large quantities of hydrogen peroxide were formed, the usually expected trimolecular impacts seemed inadequate. The bimolecular process proposed seems possible, since the usual prohibition applies to the interaction of atoms only. In the present case there should be sufficient opportunity for the energy of the process to be taken up within the internal degrees of freedom of the product.

Later Campbell and Rodebush (162) demonstrated that the whole reaction takes place in the liquid-air trap. A dry-ice trap interposed between the discharge and the liquid-air trap should catch any peroxide coming from the discharge or regions just beyond it. None was found in this trap, and the yield in the liquid-air trap was as high as ever, showing that the active species will not react at −78° C. nor will it condense at that temperature. Geib (165) points out that the results of Campbell and Rodebush are in agreement with the work of Geib and Harteck (104, 134). Harteck (136) and Willey (146) further discuss the chemistry of hydroxyl.

Oxidation by hydroxyl. We have seen that atomic oxygen exhibits very little tendency for reaction with carbon monoxide (see above). The process

$$O + CO + (M) \rightarrow CO_2 + (M)$$

is very inefficient (77, 91, 137). It is therefore interesting to note that Jackson (152) showed that the products of the water-vapor discharge can oxidize carbon monoxide even when drawn several centimeters from the discharge. Hydrogen atoms most likely assist in bimolecular collisions and react:

$$H + O_2 + CO \rightarrow CO_2 + OH$$

or the process may take place in two steps

$$H + O_2 \rightarrow HO_2;\ HO_2 + CO \rightarrow CO_2 + OH$$

or

$$H + CO \rightarrow HCO;\ HCO + O_2 \rightarrow CO_2 + OH$$

But these reactions involving hydrogen atoms are not the only possible ones leading to carbon monoxide oxidation. To some extent the reaction

$$OH + CO \rightarrow CO_2 + H$$

may be taking place, although the amount of hydroxyl present seems inadequate to account for the whole oxidation. The hydrogen peroxide formed is recoverable in large quantities and may be produced by a chain reaction postulated by Taylor and Marshall (24):

$$H + O_2 \rightarrow HO_2;\ HO_2 + H_2 \rightarrow H_2O_2 + H,\ \cdots \text{etc.}$$

The whole complex of reaction possibilities has not been completely elucidated, although some of the latest work to be discussed presently has furnished evidence for the long life of hydroxyl and it will be necessary to consider its intermediary action in many processes.

Post-discharge reactions of hydroxyl. The behavior of hydroxyl radicals after the generating discharge through water vapor was interrupted was studied with great care by Oldenberg (138, 155, 172) and Frost and Oldenberg (164). OH bands could be observed in absorption at least one-eighth of a second after the discharge was cut off, while their emission spectra died out with the current. Using the latest refinements of modern spectroscopy, they were able to estimate the relative concentration of hydroxyl as a function of time and hence determine the rate of their disappearance. The influence of different water-vapor pressures and the addition of helium gave information of the importance of triple collisions. Potassium chloride surfaces increase the rate of the hydroxyl recombination as already shown by Taylor and Lavin (83). No appreciable concentration of hydrogen peroxide is built up during the time of observation. Ions will have recombined after a few thousands of a second after the discharge is interrupted, and they will therefore play no part in these post-discharge reactions. Water molecules, hydroxyl radicals, hydrogen atoms and sometimes helium atoms will be present in the discharge. Atomic oxygen is known to be absent if the discharge current used has not been too high. Likely reactions between these species are:

I. Trimolecular processes:

$$H + H + (M) \rightarrow H_2 + (M) \quad (M) = \text{particle} \tag{1}$$

$$H + OH + (M) \rightarrow H_2O + (M) \tag{2}$$

$$OH + OH + (M) \rightarrow H_2O_2 + (M) \tag{3}$$

II. Bimolecular processes:

$$H + OH \rightarrow H_2O \qquad (2a)$$

$$OH + OH \rightarrow H_2O_2 \qquad (3a)$$

The first set would indicate removal of hydroxyl radicals at a rate

$$-\frac{d[OH]}{dt} \qquad k_3[OH]^2[M] \qquad (4)$$

and further terms if more than one kind of particle M is effective as a third body. If hydrogen atoms and hydroxyl radicals are primary products and are removed at about the same rate, then

$$[H] \doteq [OH] \quad (5) \quad \text{and} \quad \frac{d[}{dt} = k[OH]^2[M] \qquad (6)$$

which relation on integration indicates that the reciprocal of the hydroxyl radical concentration is proportional to the time, a relation found by experiment. The set of reactions (2*a*), (3*a*) yield a similar relation, and (M) may be the wall of the reaction vessel. Experiments with varying amounts of water vapor and/or helium indicate that the reaction is trimolecular ([2], [3]). The next question is whether reaction (2) or (3) takes place. If hydrogen peroxide is formed in any concentration according to (3) it should be possible to observe its absorption spectrum at $\lambda = 3100$ Å (65). None was formed, even though 0.01 mm. of hydrogen peroxide could have been detected. It may be decomposed as soon as formed (133, 162):

$$H + H_2O_2 \rightarrow H_2O + OH \quad (7); \quad OH + H_2O_2 \rightarrow H_2O + HO_2 \quad (8)$$

It would appear then that the main reaction in the post discharge is (2):

$$H + OH + (M) \rightarrow H_2O + (M)$$

The disappearance of hydroxyl radicals by reaction with hydrogen peroxide (8) was investigated by Frost and Oldenberg (164). They studied the absorption of hydroxyl radical in a discharge filled with hydrogen peroxide, after the current had been cut off. Urey, Dawsey and Rice (65) had found that in a weak discharge through hydrogen peroxide only the OH bands appeared, indicating the absence of atomic hydrogen and oxygen. Such a weak discharge offers therefore an opportunity of observing the interaction of

$$OH + H_2O_2 \rightarrow \text{Products}$$

with a fair possibility of hydroxyl radicals also reacting among themselves.

After the discharge through hydrogen peroxide had been interrupted, the OH bands disappeared much more rapidly than in the similar experiment in water vapor. Hydroxyl radicals were present because their emission spectrum is even stronger in the present than in the former experiment. It seems plausible to assume that they are removed by a bimolecular process, perhaps

$$OH + H_2O_2 \rightarrow H_2O + HO_2$$

because of its rapidity. However, even so only a small fraction of all the bimolecular collisions leads to reaction. The actual products are not known, but may be water molecules. In summarizing the primary processes taking place in electrical discharge, Oldenberg (155) points out that the production of hydroxyl is brought about by electron impact:

$$H_2O \rightarrow H + OH \ (1); \text{ or } H_2O \rightarrow H^* + OH \ (2); \text{ or } H_2O \rightarrow H + OH^* \ (3)$$

The probable post-discharge reactions are:

$$H + H + (M) \rightarrow H_2 + (M) \ (4); OH + OH + (M) \rightarrow H_2O_2 + (M) \ (5)$$

$$H + OH + (M) \rightarrow H_2O + (M) \qquad (6)$$

Reaction (6) is slower than (5), or else the large amount of H_2O_2 obtained under certain conditions cannot be understood. The reaction

$$OH + OH \rightarrow H_2O + O$$

is unlikely, for atomic oxygen is not found in large enough concentrations. Hydrogen peroxide disappears:

$$H_2O_2 + H \rightarrow H_2O + OH; \ H_2O_2 + OH \rightarrow H_2O + HO_2$$

But the reaction:

$$OH + H_2 \rightarrow H_2O + H$$

requires 14 k-cal. for activation and hence will not occur at room temperature (103). The reactions considered take into account only normal radicals and atoms, though it is obvious that excited molecules, radicals and atoms are being produced in the discharge. These energy-rich species may well have special reactivity, so that they may undergo reaction even during their short lives if the pressure is high enough so that they may suffer a sufficient number of impacts.

Atomic halogens. It is known that the halogen molecules can be dissociated by radiations of appropriate frequency and by thermal means. The resulting atoms have been considered in many reaction mechanisms. We need only mention the hydrogen-chlorine reaction (85). It is to be expected that dissociation will also occur in electrical discharge. Experiments of this latter kind were performed by Rodebush and Klingelhoefer (109, 125), who used an electrodeless discharge of not too high frequency (Fig. 56). They observed that the catalytic effects of the walls, water, metals, etc., are different for each system such as atomic hydrogen, oxygen, chlorine or hydroxyl, etc. The catalytic activity for chlorine recombination was studied by the method of Bonhoeffer (14). Silver and copper gave signs of catalytic behavior for chlorine atom recombination, but aluminum and nickel did not. Salts like sodium chloride and potassium chloride were erratic in behavior. The heating effects and the pressure difference produced at a diffusion gauge showed that chlorine atoms and not complex molecules were produced.

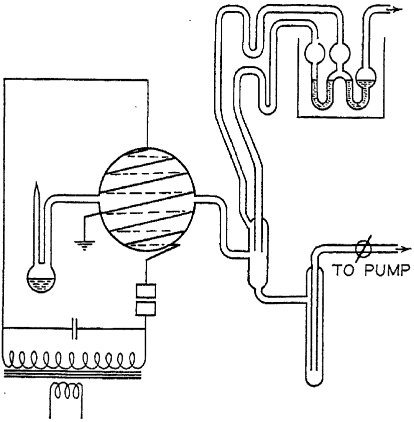


Fig. 56.—Apparatus for study of atomic chlorine reactions. Rodebush and Klingelhoefer, J. Am. Chem. Soc. 55, 130 (1933).

Chlorine atoms and molecular hydrogen. The synthesis of hydrogen chloride has been the subject of innumerable researches as reviewed by Bodenstein (85), Kassel (106) and Semenoff (159). The present experiments of Rodebush and Klingelhoefer establish the reaction

$$Cl + H_2 \rightarrow HCl + H \qquad (1)$$

with an activation energy of about 6000 cal. Values for activation energies for elementary reactions between hydrogen and the halogens have been summarized by Morris and Pease (154). That reactions of type (1) require an activation energy has been pointed out by Franck and Rabinowitsch (72). The reaction between chlorine atoms and molecular hydrogen is a chain reaction as shown by the completeness with which it takes place when allowed to run in a fairly large volume. No difference in reaction rate was observed when oxygen gas or moisture was added. Hence some of the complicated mechanisms for the hydrogen-chlorine reaction involving water must be revised. It seems that the old atomic chain mechanism of Nernst, of which reaction (1) is a part, is a reasonable representation of the situation. The present experiments furnish strong proof for this mechanism by demonstrating the actuality of one of its steps.

Solid and gas reaction of chlorine atoms. A beginning has been made in the study of reactions involving atomic chlorine by the research just cited, and further work has been done by Schwab and Friess (127), who studied atomic chlorine reactions producing the active species in luminous discharge. They calculate an average life for chlorine atoms of 3×10^{-3} sec. Methane is very effective and chloroform less so in preventing atom recombination on the wall. While Rodebush and Klingelhoefer reported atomic concentrations up to 20%, Schwab and Friess obtained chlorine atoms up to a concentration of 40%. They studied the recombination on glass, kieselguhr, phosphorus pentoxide, chromic oxide, ferric oxide, potassium chloride, cuprous chloride, hexabromomethane, acetyl cellulose, palladium, platinum, copper, graphite, lampblack and red phosphorus and found that the recombination on any of these materials requires no heat of activation. Metals, red phosphorus and chromic oxide are especially active catalysts.

Oxygen added beyond the discharge to the flowing gas has no influence on the concentration of chlorine atoms. Other gases such as hydrogen, methane, carbon monoxide, chloroform and nitrous oxide were studied in their effect on the atom concentration.

Atomic bromine. Using the method of Schwab and Friess (127), Schwab (141) succeeded in producing atomic bromine and identifying it by spectrographic means. The average life of bromine atoms in the flowing gas is 1.8×10^{-3} sec. Recombination takes place on every collision on the wall and is independent of the wall material (copper, glass, picein). Methane had much less influence in poisoning the wall for recombination of bromine atoms as compared with its effect on chlorine. The concentration of bromine atoms reached is estimated to be from 10 to 40%.

The recombination of halogen atoms is of very great importance to the understanding of the mechanism of many photochemical and thermal reactions. ·The problem has been discussed lately by Hilferding and Steiner (151), Rabinowitsch and Lehmann (156) and Rabinowitsch (168). Further use of the type of experiment in flow systems producing halogen atoms in electric discharge should furnish much needed information pertaining to the chemical behavior of these atomic species.

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PART II

THE CHEMICAL REACTIONS IN ELECTRICAL DISCHARGES

CHAPTER VII

HYDROGEN AND HYDROCARBONS (1 TO 1.6)

(1) **Active Hydrogen and Hydrogenation.** In 1866 Berthelot (1) examined the reactivity of hydrogen toward other gases in the spark. He found that cyanogen gave some acetylene. Carbon bisulphide also gave acetylene, though more slowly than cyanogen, and decomposed in part, liberating sulphur. Carbon monoxide and hydrogen, in the absence of water and carbon dioxide, on prolonged sparking gave a little acetylene.

Chabrier (2) claims that hydrogen, passed through an ozonizer, attains an activity that can be transported outside the tube, producing ammonia in air and reducing fresh silver oxide to form a hydrogen compound of silver.

P. and A. Thenard (3) found that a mixture of carbon monoxide and hydrogen unites in the silent discharge (effluve) to give an oleaginous liquid. They warn against believing with Brodie (4) that the reaction is so simple as to consist of the reduction of carbon monoxide to methane, accompanied by an addition of hydrogen and carbon monoxide to give formic acid. In sparking carbon dioxide and hydrogen, Brodie also observed a few oily drops.

Brillot (5) also subjected hydrogen and cyanogen to electrical discharge and obtained hydrocyanic acid and other unidentified products which he does not describe.

Berthelot (6) studied the action of hydrogen subjected to silent discharge upon a number of organic liquids and gases. He reported the reduction of benzene to C_6H_8 and the hydrogenation of turpentine. He found that acetylene polymerized in the presence of hydrogen much as when alone, but about 20% of the hydrogen nevertheless was absorbed. (This corresponds exactly to recently published results of Lind and Schultze (123).) On heating the solid polymer (from 100 volumes of acetylene and hydrogen), Berthelot obtained 4 volumes of ethylene, 6 of ethane and 90 of hydrogen. In another experiment, Berthelot obtained the liquid polymer found by Thenard which gave the reactions of styrolene.

Figuier (7) examined the reactions of hydrogen in silent discharge with various agents and obtained the following: $S \rightarrow H_2S$; $Se \rightarrow H_2Se$; P (ordinary) $\rightarrow PH_x$ (inflammable); $N \rightarrow NH_3$; $KHC_2O_4 \rightarrow$ formate; HAc → EtOH. Te, As, Sb and red P gave negative results.

In studying various reactions of carbon monoxide and carbon dioxide which will be described later under carbon, Berthelot (8) paid especial attention to those with hydrogen in the effluve. In a mixture of 100 volumes of carbon monoxide and 244 of hydrogen treated for 24 hours, all the carbon monoxide was found to have reacted with an equal volume of hydrogen without the formation of any carbon dioxide or acetylene. The condensed product was a mixture of polymers partly soluble and partly insoluble in water, of the general formula $(CH_2O)_n$ or $(CH_2O)_n - H_2O$. The solution of water-soluble products reduced ammoniacal silver nitrate. In excess of carbon monoxide ($100\ CO : 50.6\ H_2$) all the hydrogen had disappeared in 24 hours, leaving 23.3 volumes of carbon monoxide, the condensation ratio being $3CO : 2H_2$ or $H_4C_3O_3$, the ratio of pyruvic acid. On evaporating the water solution, the residue carbonized with a caramel odor. The same was observed in the 1 : 1 carbon monoxide-hydrogen mixture.

In a mixture of 100 parts of carbon dioxide to 220 parts of hydrogen after prolonged treatment in effluve, there were left 3 parts of carbon dioxide and 27 parts of hydrogen and a condensed product $(CH_4O_2)_n \rightarrow (CH_2O)_n + n\ H_2O$, a syrupy liquid with an odor of acetic acid which was quickly lost by evaporating. The residue carbonized with a caramel odor. It gave no test for formaldehyde. Some carbon monoxide was formed as an intermediate product which later disappeared.

In a mixture of 100 parts of carbon monoxide, 216 parts of hydrogen and 113 parts of nitrogen, treatment for 24 hours left no carbon monoxide, carbon dioxide, hydrocarbon or ammonia. There had reacted: 100 parts of carbon monoxide, 147.1 parts of hydrogen and 48.4 parts of nitrogen, corresponding to $(CHO \cdot NH_2)_n$ or $(CNH)_n \cdot m\ H_2O + (n - m)H_2O$. In a 2 : 3 : 1 mixture of carbon monoxide, hydrogen and nitrogen after 24 hours no carbon monoxide, carbon dioxide, hydrocarbon or ammonia remained. The product had the formula $C_5H_4N_4O + 4H_2O$, corresponding to sarcine, which seems merely a coincidence.

In a mixture of 100 parts of carbon dioxide: 200 hydrogen: 114 nitrogen there remained after treatment 13.5 H_2, 64.8 N_2, no carbon monoxide or carbon dioxide. Reacted to $CH_{3.73}NO_2$ or $CONH_2 \cdot H_2O$ roughly.

In 1901 Berthelot (8) examined the influence of the spark on hydrogen and reported no effect.

In 1915 Koenig (9) did not succeed in demonstrating any activity of hydrogen outside of the path of electrical discharge in it.

Paneth (10), in the preparation of tin hydride (SnH_4) by sparking in hydrogen, observed that it is necessary to have a small amount of hydro-carbon gas present to obtain the hydride.

Venkataramaiah (11) reported that hydrogen after passage through an ozonizer would reduce phosphorus and sulphur. He favored the hypothesis of H_3. Newman (12) found the hydrogen is absorbed by a cathode coated with phosphorus, sulphur or iodine, and also (13) by sodium, potassium and sodium-potassium alloy. Hydrides were proved by chemical analysis in the reactions with sodium, potassium and sulphur. Similarly Rusk (14) observed that hydrogen is absorbed by potassium in the low-pressure arc above 12 volts, very strongly at 16 volts, the arc appearing violet and giving hydrogen lines. No absorption occurred between 6 and 8 volts. Later Rusk showed that hydrogen at low pressure and potassium vapor form potassium hydride at 16 volts in the low-pressure arc, the more rapidly the higher the temperature.

In 1904 de Hemptinne (15) announced the reduction of oleic to stearic acid by hydrogen in electrical discharge (effluve). He found the yield better at reduced pressures of hydrogen, which is readily understood on account of the easier passage of discharge at low pressure, when the free path of the electron becomes sufficiently long to favor new ionization by collision. This was the beginning of a series of important discoveries (and patents) by de Hemptinne on the effect of electrical discharge on liquid hydrocarbons, which will be described later under carbon compounds and the "Voltol Process" (page 323).

In 1919 de Hemptinne (16) studied in detail the reduction of unsaturated oils by hydrogen at reduced pressure in electrical discharge and the consequent decrease in iodine number. At constant gas pressure the reaction increases with heat, but less than proportionately to the voltage. For not too different current densities the reaction increases in proportion to the current; when current densities are very different, the increase of reaction is less than proportional to the current.

The reduction of metallic oxides placed on one of the electrodes in discharge in hydrogen was also studied by de Hemptinne (17). Using PbO_2 powder as a standard of comparison he examined PbO, MnO_2, HgO, CuO, NiO, Fe_3O_4, Al_2O_3. NiO and Al_2O_3 were not reduced at all and CuO only very slowly. He also tested HgCl, $HgCl_2$, AgCl, HgBr, HgI_2, KI (very slow), As_2O_3, $SnCl_2$, Sb_2S_3, $KClO_3$, $KMnO_4$ (not reduced), C_2Cl_6 and $CuSO_4$ (not reduced). The use of carbon monoxide as a reducing agent under similar conditions will be described in (6.8).

The electrical behavior of hydrogen in a Siemens tube operated at high frequency was investigated by Lunt (II, 17), who gave an analysis which affords determination of the voltage gradient and of the current carried by the ions in hydrogen. An attempt was made to calculate the approximate mean intensity of ionization in hydrogen under any given electrical conditions by relating the conducting current in the ionized gas to the known motion of ions and electrons in hydrogen and to the impressed electrical force.

Anderegg and Herr (VI, 17) in 1925 published results of experiments in activating hydrogen in the so-called " creeping corona." A corona discharge tube was packed with glass wool, which was found to assist in the activation of hydrogen. At a flow of 40 cc. per minute the active hydrogen then passed through 5 cm. of 1-cm. glass tubing and 50 cm. of 5-mm. tubing before coming into contact with nitrogen, with which it combined to form ammonia which was dissolved and determined by nesslerizing.

Wendt and Landauer (VI, 6) had previously studied the activation of hydrogen both in low-pressure discharge and in corona. From the positive results of these experiments, which demonstrated a transportable form of activity of hydrogen with respect to sulphur, arsenic, phosphorus, mercury, nitrogen and acid and neutral permanganate solution, they derived support for triatomic hydrogen (H_3) which Duane and Wendt (VI, 5) had first encountered in their activation and condensation of hydrogen by alpha rays. (Further reference to this subject and to subsequent work by others will be found later in this section.)

In 1921, Wood (VI, 7) discovered the very important method of producing atomic (chemically active) hydrogen by means of luminous discharge in hydrogen at a pressure of a few tenths of a millimeter of mercury. He identified the Balmer lines as associated with atomic hydrogen and the bands or multi-line spectrum as belonging to molecular hydrogen. He observed the recombination $2H \rightarrow H_2$ to be variously catalyzed by different metals, for example, tungsten, aluminum and platinum. The heat of recombination at the surface of a tungsten wire will cause it to glow brightly. This is a convenient method of detecting the presence of atomic hydrogen which has under favorable conditions a life of an appreciable fraction of a second and can be transported some distance from the point of dissociation. He also confirmed Langmuir's discovery that water vapor in the gas poisons the wall against catalytic recombination of hydrogen atoms and thus favors high concentration of the atomic form. In general, the properties which he found for atomic hydrogen produced electrically were in accord with those which Langmuir (VI, 22, 27, 29, 46) had found by thermal dissociation and which he applied so successfully in hydrogen arc welding.

Bonhoeffer (VI, 14) made a systematic study of the chemical properties of atomic hydrogen dissociated in the luminous discharge according to Wood. Among solids he tested the oxides, sulphides and halogen salts of a number of metals with the results shown in Table 11.

TABLE 11

Action of Atomic Hydrogen on Solids

K. F. Bonhoeffer, Z. physik. Chem. **113**, 199 and 492 (1924)

	O	S	Cl	Br	I	F
Al^{+++}	−					
Mg^{++}	−		−			
Cr^{+++}	−					
Fe^{++}			−			
Co^{++}			−			
Ni^{++}			−			
Zn^{++}	−		−			
Cd^{++}		+	−		+	
Cu^{+}	+	+	+			+
Cu^{++}	+	+	+			+
Pb^{++}	+		+			
Bi^{+++}	+		+			
Ag^{+}	+		+	+	+	+
Hg^{+}	+	+	+			
Hg^{++}	+		+			

Note: + indicates reduction to metal; − means no change in 10 min. at 10-cm. distance from discharge.

Although the ease of reduction is evidently influenced by the heat of formation, this is not always a controlling factor. Lead chloride is readily reduced in spite of a large heat of formation, whereas ferrous chloride is not attacked at all.

Sulphur, phosphorus and arsenic were all found to be readily converted to the hydrides. Among the organic unsaturated acids hydrogenation was found to proceed readily without any attack on the carboxyl group.

Bonhoeffer arranged two ingenious devices for the quantitative study of the ratio of recombination of hydrogen atoms at any point in the stream. A thermometer bulb was covered with a suitable catalyst for the reaction or with any substance whose activity was to be examined and was then introduced into the active hydrogen. The rise in temperature due to recombination is directly shown. Even more sensitive was the method of covering one side of the blades of a Crookes' radiometer wheel with the catalyst and exposing to an atmosphere of atomic hydrogen. Either the velocity of rotation or the amount of torsion in the case of an element suspended by a quartz fiber is a measure of the relative ratio of recombination and of the concentration of atomic hydrogen.

Bonhoeffer found that minimal thickness of layer suffices for the catalytic monatomic layers. Besides the metals certain stable oxides such as MgO, CaO, BaO, Al_2O_3 and Cr_2O_3 are good catalysts of the recombination.

From his chemical results Bonhoeffer calculated an average life of the active form of hydrogen of about 1/3 sec. He found no discrepancy between his results and those of Wendt and Landauer, believing that at higher total pressures the active form might well be H_3.

In a final paper Böhm and Bonhoeffer (VI, 25) quantitatively investigated the reactions of active (Wood's) hydrogen with various gases. Hydrogen reacts readily with oxygen to give hydrogen peroxide of a high percentage of purity. The halogens react rapidly. Carbon monoxide and carbon dioxide react in small amount to give formaldehyde. The halogens react faster than the other gases. Active hydrogen, in a few hundredths of a second, is destroyed by hydrogen chloride, hydrogen bromide, hydrogen sulphide and methyl chloride, probably by such reactions as $H + HCl \rightarrow H_2 + Cl$ and $H + HBr \rightarrow H_2 + Br$, etc., which had already been demonstrated in the kinetic study of the thermal and photochemical syntheses: $H_2 + Cl_2$ and especially $H_2 + Br_2$, which involve them as side or opposing reactions. No activity of hydrogen atoms toward nitrogen, water, ammonia or methane could be detected.

Elliott (VI, 32) used the production of hydrogen sulphide to test for the generation of active hydrogen in the ozonizer. In the range

10–50 mm. pressure, 3–10 kv., 85–540 frequency, the time yield decreases with decreasing gas flow, increases with decreasing gas pressure, increasing voltage and power input. V_e in the equation of Elliott, Joshi and Lunt (18) is 27.9 volts. The active hydrogen obtained had a life of about 1/5 sec., did not cause tungsten wire to glow nor was its activity lost by passage through a short plug of glass wool.

The existence of an active triatomic form of hydrogen which should have a longer life and other properties different from monatomic hydrogen has been the subject of much discussion and investigation. In 1927, Paneth, Klever and Peters (VI, 36) tested various methods that had been claimed to produce triatomic hydrogen, among them ozonizer discharge as well as various thermal means and alpha rays, but all with negative results. Similarly Smallwood and Urey (VI, 49) made unfruitful attempts to produce triatomic hydrogen by various means including both corona and ozonizer discharge. Since the formation of hydrogen sulphide on the passage of active hydrogen over sulphur had been extensively used as a critical test, they paid especial attention to refining its detection by absorption in silica gel at liquid-air temperature. The great difficulty of obtaining satisfactory blank tests for hydrogen sulphide threw doubt on the validity of its previous use as criterion of triatomic hydrogen. They found that most flowers of sulphur contain volatile sulphides. Paneth and his co-workers had also found it difficult to obtain good blanks and suggested that the glass walls of the discharge tube are often a source of sulphur capable of generating hydrogen sulphide. Curtius (19) also failed to obtain any transportable active form of hydrogen in the ozonizer.

Elliott (VI, 32) reasserts the formation of active hydrogen, stating that the claims of Willey and himself to activate hydrogen in a form other than atoms at extremely low pressure are the only ones that can be regarded as valid. He rejects the suggestion of Smallwood and Urey (VI, 49) that his activation may have been due to sulphur dust blowing back into the discharge itself.

On the other hand there is no question as to the contraction of hydrogen observed by many both in electrical discharge and under alpha radiation but it is probably due to fixation of hydrogen by reaction with the glass wall or in some other way rather than to the formation of a stable H_3. Taylor (20) demonstrated the loss of hydrogen to the wall in electrical discharge at 300 volts at the rate of one hydrogen molecule per electron flowing. Later (21) he subjected hydrogen to electrodeless discharge in glass at pressures from 2 mm. down and collected water (in a liquid-air trap) the oxygen of which must come from the glass. Thomson (22) also mentions the clean-up of hydrogen in electrodeless discharge and the formation of arsenic hydride. Delaplace (23) confirmed the contraction of hydrogen in electrical discharge but did not attribute it to the formation of triatomic hydrogen. Most of the contraction occurs in the first quarter of an hour and amounts to 4 to 4.7%. He also found methane and carbon monoxide to be present after discharge although he was operating in the absence of stopcocks.

Schwab and Seuferling (VI, 48) produced hydrogen sulphide and arsenic hydride by passing hydrogen after activation in silent discharge at 50-mm. pressure over sulphur and arsenic. They used a micromethod by freezing hydrogen sulphide in a glass capillary at liquid-air temperature and measuring the volume over mercury at room temperature. The amount of hydrogen sulphide thus obtained exceeded the blanks (without sulphur) by tenfold.

v. Wartenberg and Schultze (VI.67) studied the reactions of atomic hydrogen produced by Wood's method toward the lower hydrocarbons in gaseous mixtures. Methane was not attacked but imparted slight catalytic properties to the hydrogen in hydrogenation reactions. Ethane and acetylene also remained unchanged but strongly catalyzed the hydrogen. Ethylene was hydrogenated to ethane with the production of some acetylene and strong hydrogen catalysis.

v. Wartenberg and Schultze (VI, 67) later discovered that oily phosphoric acid when wiped on the glass wall of the discharge tube has a strong poisoning effect which prevents the recombination of hydrogen atoms and thus enhances the concentration of active hydrogen. Schultze and Müller (VI, 79) found that hydrogen passed over metallic lead formed a hydride which was decomposed at red heat with formation of a lead mirror.

Foresti and Mascaretti (24) succeeded in preparing hydrides of tin, bismuth and lead in a current of pure hydrogen (without hydrocarbons) which was activated by oscillatory discharge. The yield was not dependent on the period of oscillation. The best results were obtained with tin electrodes at a small distance of separation.

Aono (25) used a modified ozonizer consisting of four concentric tubes in which the activated hydrogen passes immediately through the liquid to be acted on. He hydrogenated cod-liver, fish, olive and silkworm pupa oils as well as oleic acid.

Schumb and Hunt (26) employed electrodeless discharge for the activation of hydrogen and other gases for the reduction of various substances placed directly in the discharge tube with hydrogen at a pressure of a few millimeters or lower. Sulphur, iodine, potassium ferricyanide, cupric chloride hydrate, sodium and calcium were reduced in the solid state. Azoxybenzene was reduced through the successive stages: azobenzene → hydrazobenzene → aniline; *p*-nitrotoluene was reduced at 9 mm. to *p*-toluidine. Mixtures of hydrogen and nitrogen 3 : 1 combined to form ammonia up to a little over 30% ammonia yield, where synthesis seemed to stop, indicating an equilibrium which was confirmed by measuring the decomposition of ammonia, which stopped at 67.2%.* It is notable that this equilibrium is different from that of 20% ammonia yield found by many authorities in other types of discharge. (See [7.1].)

Schwarz and Royen (27) concluded from a study of the contraction of hydrogen in silent discharge at liquid-air temperature that it is due to surface condensation of atomic hydrogen and that there is no evidence of triatomic hydrogen. Schultze (VI, 96) also rejected the hypothesis of triatomic hydrogen. Hiedemann (VI, 92; 28) in a very careful review of the literature and in his own experiments could find no evidence for triatomic hydrogen. He did find, however, that the condensible gas sometimes mistaken for atomic hydrogen is silicon hydride (SiH_4) (or sometimes Si_2H_6) from the reduction of silicon dioxide in the glass or silica wall of the discharge vessel. Mierdel (29) showed that this gas can cause a number of reductions attributable to active hydrogen or to hydrogen sulphide such as reduction of tungsten oxide to blue or green, and the precipitation of lead acetate solution. It also reacts with Nessler's reagent, confusing the ammonia test, and reduces indigo blue solution to indigo white.

Using potash glass and spodumene as anode sources of K^+ and Li^+ gas ions, respectively, Kunsman and Nelson (30) found that the rate of clean-up of hydrogen is independent of the number of ions entering the gas phase but varies with the electrolytic potential between the glass anode sheath and its platinum ribbon core, and is therefore due to the formation of water at the surface.

Glockler and Thomas (V, 34) dissociated the hydrogen molecule at a pressure of 0.02 mm. sensitized by mercury vapor at a pressure of 0.002 mm. under bombardment by electrons of controlled speed. The reaction threshold was observed at 7.7 volts instead of 4.9 volts, the resonance level of mercury. The sequence of reactions is given in Chapter V, page 98.

Delaplace (31) discovered that hydrogen does not disappear in a discharge tube if perfectly dry. He offers the explanation that no hydrogen atoms are present on account of their well-known recombination on the dry wall.

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* Later in a vacuum tube oscillator the decomposition in some cases was carried close to 100%.

Srikantan (32) found that hydrogen is reversibly absorbed in a high-frequency oscillator, while ammonia is irreversibly absorbed since it decomposes into the elements as soon as the apparatus becomes saturated with ammonia.

(1.6) **Hydrocarbons.** The hydrocarbons have been repeatedly investigated from the earliest time when spark discharge became available. Although decomposition, even to the point of depositing free carbon, is often observed particularly in spark discharge, the tendency toward condensation and polymerization even to form liquid and solid products is one of the most interesting and striking characteristics of the chemical effects that accompany electrical discharge in hydrocarbon gases.

This tendency to condense in electrical discharge to form larger molecules is not confined to hydrocarbons but extends to their derivatives and also to most organic compounds, especially the unsaturated ones, and is found even in some non-carbon compounds such as sulphur dioxide, but is not prominent in non-carbon hydrides such as ammonia and hydrogen sulphide.

Fourcroy (33) in 1796 subjected three different kinds of unspecified hydrocarbons obtained from alcohol and ether to sparking. He obtained oily droplets without depositing carbon, and found that the volume of gas increased by two-fifths. In 1798 Henry (34) observed the condensation of "gaz hydrogené carboné" by sparking. In 1809 Dalton (35) also observed the decomposition of hydrocarbon gases in the electric spark. Henry (34) and Quet (36) also noted the re-formation of carbon and the expansion of gaseous hydrocarbons under sparking.

In 1869 Berthelot (37) subjected methane to the spark and observed deposition of carbon, liberation of hydrogen, the formation of acetylene and increase of volume from 1 to 1.8. Later Berthelot (38) distinguished between the formation of amorphous carbon which he attributed to the thermal decomposition of methane by spark and the formation of a small amount of graphite which presumably is of electrical origin.

In 1860 Buff and Hofmann (39) cite the earlier work of Dalton, Davy and Bischoff and report that the decomposition of methane is slow in the spark, much faster in the arc. In 1873 P. and A. Thenard (40) confirmed the decomposition of methane in the spark and also observed the addition of methane and carbon dioxide to form a liquid which turned to amber color in the course of time. In 1874 de Wilde (IV, 43) using the Siemens tube to examine the behavior of ethylene in silent discharge found rapid polymerization to a liquid with odor of petroleum and turpentine.

Both the formation and reactions of acetylene in electrical discharge have attracted much attention. Berthelot (41) found it could be produced in small quantity by sparking methane and that it could be synthesized from the elements in the arc but not by the spark. He further found it could be obtained from any hydrocarbon in the high temperature of the spark and in much smaller quantity in silent discharge, exactly the opposite of ozone. Later Berthelot (42) found that sparking of methane for a few hours forms 12.5% of acetylene, representing a yield of 50%.

The decomposition of acetylene was found by Berthelot (43) to be brought about by the induction spark, which was confirmed by Morren (44). It was found by Truchot (45) that the spark immersed in liquid hydrocarbons produced decomposition to simpler gases. In 1869 Berthelot (46) claimed that an equilibrium is attained in the spark: $C_2H_2 \rightleftharpoons 2C + H_2$, which varied stepwise with continuously varying pressure. Naturally this claim would now meet with much doubt.

The polymerization of acetylene by electrical discharge has often been investigated. In 1874 de Wilde (IV, 43) found that acetylene polymerizes more readily in the ozonizer than does ethylene but that no benzene was formed as might have been expected from Berthelot's thermal experiments. The product was a yellow, oily liquid that formed on the wall where it was traversed by the current, which may explain its later solidification to a hard, brittle, brown amorphous solid for which no solvent could be found. The solid burns on platinum leaving a residue of porous charcoal. No gaseous residue was left in the condensation. P. and A. Thenard (47) reported that the polymerization of acetylene to a solid occurs with ease, while the polymerization to liquid takes place more difficultly and under special conditions which were not specified. Parenthetically, it may be said here that all the recent experiments of the present authors and their co-workers resulted only in the direct production of solid polymer.

On studying the reactions of methane, ethane and ethylene in silent discharge (effluve), Berthelot (48) found that all give acetylene in small quantities, free hydrogen and condensed or polymerized hydrocarbons. Too little liquid was obtained from methane to be collected. Ethylene gave a liquid $C_nH_{1.83n}$ and a little benzene.

In 1890 Berthelot (49) made a further examination of the polymer of acetylene produced in ozonizer discharge and found it to be very different from the polymer produced from acetylene thermally at 400–500° C. The latter is formed with a loss of 171,000 cal., is quite stable and has the character of benzene. The electrical condensate retains more energy, decomposes explosively, oxidizes spontaneously in air, gaining one-quarter of its own weight in several weeks. It is a varnishlike solid, yellow to brown in color, which can sometimes be stripped from the wall in a thin film. It continues to alter with age and possesses some volatility which gives it a tendency to form new deposits at a distance. Under distillation the polymer decomposes almost explosively to free carbon and a residue which forms acid on addition of water. Distillation with lime gives simpler products, especially acetone.

De Hemptinne (50) subjected benzene to weak alternating discharge and obtained a gummy waxlike material, some hydrocarbon gases, a little acetylene and hydrogen.

In 1899 Berthelot (51) continued the study of the condensation of unsaturated hydrocarbons in the ozonizer. Acetylene polymerized first to a liquid and then to a solid which decomposed explosively on heating. Complete polymerization leaves a small residue of hydrogen (1.8% of original), of ethylene (0.8%) and 0.08% ethane. The solid polymer absorbs oxygen rapidly from the air. Propylene condenses rapidly to liquid, completely in a few hours. One hundred volumes of propylene gave 34.2 of hydrogen, 0.7 of methane and a liquid $C_{15}H_{26}$ which he thought significantly near $(C_3H_5)_n$.

Trimethylene was found to undergo the same type of condensation, though sensibly more slowly than propylene. One hundred volumes yielded 37.3 volumes of hydrogen, 1.5 of methane and again a liquid $C_{15}H_{26}$.

Allylene condenses rapidly, with evolution of very little hydrogen, to a liquid with a sharp empyreumatic odor, very slightly volatile at ordinary temperature and having the empirical formula $C_{15}H_{19}$.

In 1901 Berthelot (52) observed that acetylene decomposed so rapidly in the electric spark that frequently carbon bridged across the spark gap. Excess hydrogen prevents decomposition unless the spark is chilled by a cold surface. All hydrocarbons yield acetylene in the spark in amounts easily recognizable in 1 min. Carbon monoxide mixed with hydrogen gives acetylene in the spark only upon prolonged action, which Berthelot interpreted as indicating that hydrocarbon must first be formed by the reduction of carbon monoxide.

Collie (53) condensed ethylene in silent discharge at —20° C. to a liquid which boiled at 130–170° C. About 20% of hydrogen was liberated. Six fractions were obtained by distillation, the largest at 100–150° and 150–200°. Methane and carbon monoxide formed an addition product that gave a test for aldehyde.

Losanitsch and Jovitschitsch (54) examined unsaturated hydrocarbons in silent discharge and found polymerization and condensation. Ethylene gave a yellow liquid boiling above 200° C. Benzene yielded a gummy polymer. Their results were similar to those of P. and A. Thenard, who in 1873 had obtained from ethylene in the ozonizer a colorless liquid with strong odor which was insoluble in water but readily soluble in ether. It may be remarked in general that color seems to be associated with secondary action of discharge on liquid hydrocarbons before removal from the field.

About ten years later in 1907 Losanitsch (55) published a very extensive investigation of various hydrocarbon reactions under influence of electrical discharge. He found that the polymerization product from acetylene consists of two parts, one soluble in alcohol and ether, the other a solid insoluble in all solvents. He found both to be rapidly decomposed on drying at 100° C. Analyses for carbon and hydrogen do not give a 100% total, which he attributed to addition of oxygen from the air. He also claimed the evolution of a non-radioactive emanation which could oxidize solution of potassium iodide and act on the photographic plate through several sheets of aluminum or gold foil.

Acetylene and water vapor combined to form acetaldehyde which polymerized and formed an addition product with acetylene which remained soluble in water. The molecular weight of the product was found to be 577, whereas the molecular weight of the fivefold polymer $(3C_2H_2 \cdot C_2H_4O)_5$ would be 610.

Acetylene and hydrogen gave two condensation products which behaved much like those obtained from acetylene above. This would be expected from the result later obtained by Lind, Bardwell and Perry (56) under alpha radiation, which showed that the product of the polymerization of acetylene is uninfluenced by the presence of hydrogen but that the rate is increased by the amount of ionization which hydrogen contributes. The soluble fraction Losanitsch thought to be $(C_2H_2 \cdot 2C_2H_4)_2$. The insoluble portion has a higher molecular weight.

A mixture of methane and acetylene gave the same condensation products as acetylene and hydrogen except that the soluble portion becomes the greater.

Acetylene and ethylene also form a soluble and an insoluble portion. In the combination of acetylene and hydrogen sulphide, the insoluble portion predominates. Acetylene and carbon monoxide unite to form a yellowish brown solid which is insoluble, possesses a burnt smell, decomposes on heating and takes up oxygen readily to form a final product with the empirical formula $4C_2H_2 \cdot CO \cdot O_2$. Acetylene and sulphur dioxide combine to form a dark brown insoluble substance of the formula $C_2H_2 \cdot SO_2$.

Ethylene yields a yellow to reddish liquid which is soluble in alcohol and which boils above 260° C. The liquid accepts oxygen from the air to form a compound of formula $(C_{12}H_{22}O)_2$, whose molecular weight 364 agreed fairly well with the formula weight 400. Ethylene and methane were found to combine in a thick yellowish red liquid which took oxygen from the air to form a compound with the empirical formula $C_{22}H_{42}O_4$.

Ethylene and hydrogen sulphide formed a thick yellow to red liquid with an odor of mercaptan which was soluble in benzene and in carbon bisulphide but insoluble in alcohol; of formula $(C_2H_4S)_6 = 360$; experimental molecular weight 400. The reaction is formulated as follows:

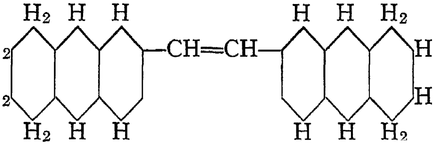
$$C_2H_4 + H_2S \rightarrow C_2H_5 \cdot SH; \quad 6C_2H_5 \cdot SH \rightarrow (C_2H_4S)_6 + 6H_2$$

Ethyl mercaptan in silent discharge gives the same product.

Ethylene and carbon monoxide give two products: a small amount of a brown solid, and a yellow-red clear thick liquid soluble in organic solvents.

Löb (57) passed electric discharge through moist methane and obtained a white solid deposited on the wall at the rate of 0.2 to 0.3 gram in 20 hours. Its analytical formula was $C_9H_{15}O$. Traces of higher aldehydes were obtained in its aqueous extraction. The gaseous products were CO_2, C_nH_{2n}, CO, C_nH_{2n+2}.

Jovitschitsch (58) on treating ethylene in silent discharge obtained a liquid the molecular weight of which in alcohol was 420. Acetylene gave an insoluble solid, which upon bromination substituted two bromine atoms and added two also, which according to Jovitschitsch indicates the formula of the polymer to be:



About the same time Jovitschitsch (59) called attention to a mysterious deficit of carbon, as he thought, in the condensation of acetylene and ethylene.

Continuing his investigation of the behavior of hydrocarbons in ozonizer discharge, Losanitsch (60) found that benzene in air gives a thick, dark substance containing nitrogen, whereas *in vacuo* it gives first a yellow oil without liberation of hydrogen. After three days the walls were covered with a solid insoluble in ether and in benzene. The portion of the original condensate which is soluble in benzene divides itself into a portion soluble and one insoluble in ether. All three substances have the property of taking up oxygen. The formula $C_{24}H_{25}O$ is assigned to the portion soluble both in ether and in benzene. Benzene and hydrogen formed a yellow liquid soluble in ether and in benzene. A formula $C_{28}H_{34}$ was obtained for a portion containing 2.2% of oxygen. Benzene and methane gave a thick yellow-red liquid with a peculiar odor. It was soluble in ether and in benzene. The formula $C_{28}H_{36}$ was assigned to it. Experimental molecular weights found were 378 and 365; theoretical 372. Benzene and ethylene gave a thick brown-red liquid with peculiar odor, soluble in ether and benzene, empirical formula $C_{28}H_{34}$. Benzene and acetylene gave a yellowish brown solid which on treatment with benzene divided itself into a soluble and an insoluble portion. The latter is like condensed benzene. Benzene and carbon monoxide combine to a dark, thick, disagreeable-smelling liquid. Benzene and carbon bisulphide give a dark solid like the condensation product of acetylene and carbon bisulphide.

Losanitsch (61) also discovered the addition of oxygen to various condensation products, their formulas and ring structure. He attributed their effect on the photographic plate to ozone. Extending his investigations to higher hydrocarbons, Losanitsch (62) found that isopentane in the ozonizer liberates hydrogen, methane and gaseous unsaturates and an oily liquid, soluble in ether, less soluble in alcohol, which when fractionated in an atmosphere of hydrogen gave a soluble and insoluble portion. Empirical formulas were established: C_8H_{18}, C_nH_{2n}, $C_{20}H_{38}$ and $(C_8H_{14})_n$, representing various degrees of dehydrogenation. The unsaturates absorbed oxygen from the air. Hexane reacted more slowly than isopentane, which gave more unsaturates than a normal hydrocarbon. Distillation of the liquid obtained from ethylene gave fractions consisting of $C_{16}H_{30}$ and $C_{26}H_{44}$ which on standing in air took on oxygen to become $C_{16}H_{30}O$ and $C_{26}H_{44}O_2$, respectively. Benzene gave both solid and liquid. The liquid was fractionated by distillation to $(C_6H_6)_n$ and $C_{24}H_{26}$. The products from the similar treatment of benzene and hydrogen were also fractionated.

In 1914 Losanitsch (63) showed the tendency that saturated hydrocarbons have to double their chain length in electrical discharge. Also some greater multiplication occurs. Pentane gave products:

2, $C_{10}H_{20}$ and $C_{45}H_{78}$. Hexane gave similarly: (($(C_6H_{12})_3$ and $C_{36}H_{64}$. He also emphasized the rapid polymerization of the unsaturates. Ethylene gave $C_{12}H_{26}$ (clear yellow liquid); $(C_{16}H_{26})_9$ (yellow-brown solid); $(C_{16}H_{26})_n$ (yellow solid). Isoamylene gave diisoamylene, $(C_5H_{10})_4$ and $C_{45}H_{76}$. Acetylene alone gave a yellow-brown insoluble solid which was explosive above 100° C., absorbed oxygen, emitted ozone and reduced the photographic plate. Acetylene at atmospheric pressure was claimed to undergo two reactions: (1) polymerization; (2) splitting to carbon* and hydrogen, the latter combining with acetylene to give a soft soluble mass. The unsaturate $CH_3\cdot(CH_2)_4\cdot C \vdots CH$ underwent disruption accompanied by the formation of a colorless liquid soluble in alcohol, in ether and in benzene. Triheptane gave a thick odorous liquid soluble in ether and in benzene. Undecaheptine $(C_7H_{12})_{11}$ yielded a dark red thick mass soluble in ether and in benzene. The eight-carbon unsaturates $CH_3\cdot(CH_2)_5\cdot C \vdots CH$ gave dioctene $(C_8H_{14})_2$, a colorless liquid soluble in alcohol, ether and benzene respectively. Nonaoctine $(C_8H_{14})_9$ gave a dark red soft mass soluble in ether and in benzene, insoluble in alcohol. Benzene gave a number of products as follows: $(C_6H_6)_2$, $(C_6H_5)_2$, $C_{72}H_{96}$ and $(C_6H_6)_{90}$, a solid soluble in benzene, insoluble in ether and in alcohol and insoluble $(C_6H_6)_n$. Toluene gave ditoluene, a thick yellow liquid soluble in alcohol, in ether and in benzene and also dodecatoluene $(C_7H_8)_{12}$ melting at 150° C., soluble in ether and in benzene, insoluble in alcohol.

Cumene yielded two products: dicumene $(C_9H_{11})_2$, a yellow liquid soluble in alcohol, in ether and in benzene; and a brown resinous material soluble in ether and in benzene, insoluble in alcohol and melting at 95° C. All three xylenes give dixylene $(CH_3\cdot C_6H_4\cdot CH_3)_2$, a thick yellow liquid soluble in alcohol, in ether and in benzene; they also yield polyxylenes. Cymene gave dicymene $(C_{10}H_{14})_2$ and pentacymene. Mesitylene gave two products: dimesitylene $(C_6H_2(CH_3)_3)_2$ and dodecamesitylene $(C_9H_{12})_{12}$. Naphthalene polymerized to a brown, glistening, insoluble and infusible solid.

The terpenes gave liquid dimers and solid polymers which absorbed oxygen. Pinene gave di- and hepta- products, while camphene gave di- and octa- products. Limonene gave several polymers: a liquid dimer, a solid hexamer soluble in ether and in benzene and an insoluble solid of unknown degree of polymerization. Menthene gave a liquid dimer and a soft brown polymer soluble in ether and in benzene, insoluble in alcohol.

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* The present authors have never found any evidence of free carbon either in the ozonizer or in the alpha-ray treatment of acetylene.

Kohlschütter and Frumkin (64) observed that non-graphitic carbon is liberated in the gas phase by electrical discharge in hydrocarbons.

The thickening of hydrocarbons and other organic compounds by means of electrical discharge in the liquid will be considered under "Voltol Process" (page 323).

In 1924 and again in 1927 (65) Jovitschitsch emphasized the deficiency of hydrogen and carbon in the analysis of the condensation products of hydrocarbons from acetylene to limonene in spite of great precautions to avoid the absorption of either oxygen or water vapor. So strongly was he convinced of the reality of this deficiency that he suggested as possible the conversion of electrical energy into matter. Later work of Glockler and Roberts (66) gave an analytical procedure which solved the difficulties by keeping account of the amount of oxygen used in the organic combustion and offered it as a general method of determining oxygen directly instead of by the usual "difference" method.

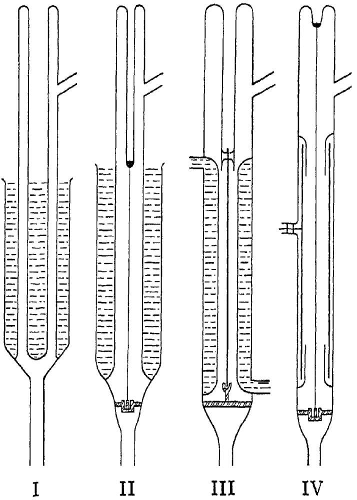

FIG. 57.—Types of discharge tubes used in the study of chemical activation of hydrocarbons.

I. All-glass ozonizer.
II. Wire semi-corona.
III. Rod semi-corona.
IV. Wire corona.

Lind and Glockler, J. Am. Chem. Soc. 50, 1767 (1928).

In 1926 Jakosky (67) studied the influence of high-voltage alternating corona discharge in the cracking of petroleum products in the vapor phase. He found that it caused the polymerization of benzene and the precipitation of hot oil vapors. He also investigated the electrical production of carbon black.

Dem'yanov and Pryanishnikov (68) applied 12 to 13 kv. on the secondary, with a current of 1 to 3 amp. in the primary circuit, to investigate the polymerization of ethylene and of isobutylene in the ozonizer. They obtained a mobile yellow-brow liquid which reacted readily with bromine to give copious fumes of hydrobromic acid. Fractionation at ordinary pressure gave fractions varying in density from 0.9048 to 0.8225 and an index of refraction from 1.4780 to 1.4568.

Fowler and Mardles (69) used the submerged spark between carbon electrodes to study the decomposition of six organic liquids and of acetylene gas: (I) paraffin oil, boiling from 182° to 300° and having a density of 0.82; (II) benzene; (III) aniline; (IV) 2-methylaniline; (V) one-methylaniline; (VI) ethyl alcohol.

TABLE 12

Decomposition of Organic Liquids by Submerged Spark

N. R. Fowler and E. W. J. Mardles, Trans. Faraday Soc. **23**, 301 (1927)

	Carbon deposit, grams per hour	Gas evolution, cc. per min.	%H_2	%CH_4	%C_2H_2	Remarks
I	0.0035	200	35	60	5	
II	0.11	200	44	53	3	
III	0.019	70	60	37	3	Little HCN; no NH_3
IV		200	50	40	3	Little HCN
V		50	70	20	5	Little HCN
VI		450	38	20	1.5	38% CO; no CO_2
VII	Acetylene—bright flash and short circuit with carbon threads.					

Moens and Juliard (70) found that acetylene and benzene, respectively, polymerize to solid products in electrodeless discharge.

In 1927 Lind and Glockler (71) began a series of investigations of the behavior of several of the lower hydrocarbons in electrical discharge tubes of various types as shown in Fig. 57. Alpha-ray studies of the same gases had already established (I, 7) the chief characteristics of those reactions, namely, that the saturates condense with evolution of hydrogen and methane to form higher members even up to liquid and solid products. The yield is constant, two molecules reacting for one ion pair, for methane, ethane, propane and butane; the gas pressure also remains constant. The unsaturates condense with a much smaller gas evolution but with a larger yield per ion pair, showing that gas liberation is by no means a criterion of the rate or extent of reaction.

The object of the experiments with electrical discharge in hydrocarbons was largely directed toward the question as to whether the same characteristics would manifest themselves as in the alpha-ray reactions. If so, then the conclusion might be fairly drawn that the same relations exist between the chemical reaction and the gaseous ionization both qualitatively and quantitatively. Since ionization in the ozonizer can neither be measured nor calculated, it was impossible to determine the ion yield. Hence the important bearing of alpha-ray yield.

The first gas to be examined, ethane, was flowed through the ozonizer at atmospheric pressure and then through a trap cooled to −5° C. to condense liquid hydrocarbons. Liquid was readily obtained at a single passage as well as hydrogen, methane and other gaseous hydrocarbons. The apparatus used is shown in Fig. 58. The fraction of hydrogen gas produced of the total hydrogen-methane mixture obtained was 0.75 in the silent discharge reaction and 0.83 in the alpha-ray transformation. The disappearance of initial ethane gas to hydrogen produced was found to be 1.4 and 1.31 for the same reactions. The liquid product in the ozonizer reaction was a reddish yellow oil of high viscosity and a penetrating odor. Its density was 0.862, and the average molecular weight 467. Its composition was found to be $C_nH_{1.8n}$ for the silent discharge and $C_nH_{1.85n}$ for radon activation.

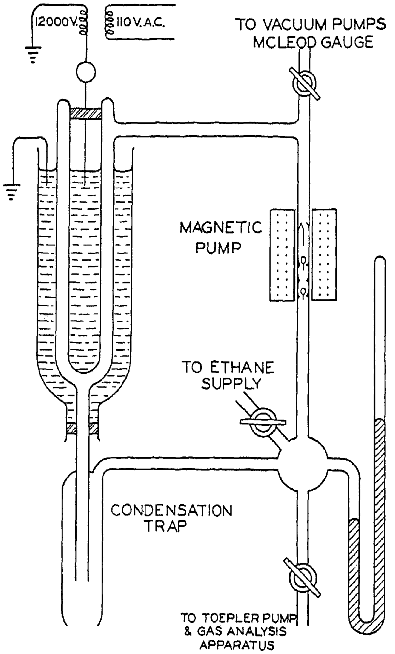

Fig. 58.—Ethane condensation in all-glass ozonizer with circulating system. Lind and Glockler, Trans. Am. Electrochem. Soc. 52, 37 (1927).

Molecular-weight control in ozonizer synthesis. The liquid product of high molecular weight and viscosity just described may have been built up from the saturated ethane in two ways: (1) by repeated doubling by means of successive ionization until a product is obtained of sufficiently high molecular weight to condense as liquid; or (2) by direct condensation of a sufficiently large number of "nascent unsaturates" (those with only one of the double bonds closed) to form the liquid directly without repeated ionization. We should expect that the first liquid droplets formed on the walls of the discharge tube would be subject to much secondary electron bombardment since the discharge in an ozonizer enters the gas phase entirely through the wall. Warming the wall should prevent condensation there. Placing a low-temperature trap in the circulating system should stop the early condensation products from returning to the discharge region, and we may expect a natural reduction in the degree of condensation or doubling of the liquid product. This situation will be revealed by the lower molecular weight of the liquid reaction product. These predictions were verified by Lind and Glockler (72). The whole circulating system with the low-temperature traps is shown in Fig. 59. The double-action circulating pump indicated has been described by Funnell and Hoover (73) and Livingston (74).

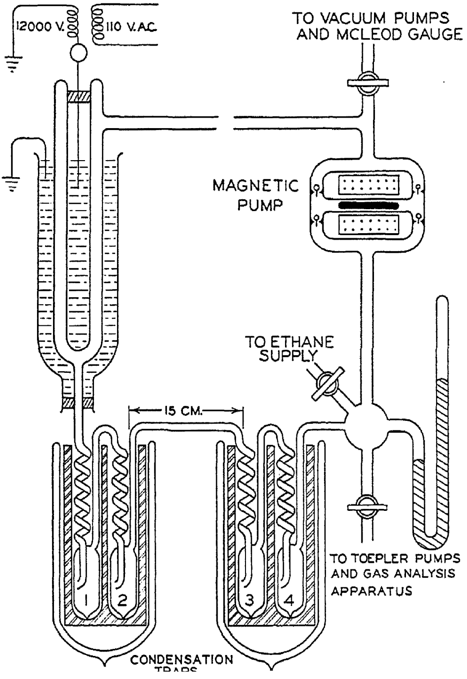
12000 V.
110 V.A.C.
TO VACUUM PUMPS AND MCLEOD GAUGE
MAGNETIC PUMP
TO ETHANE SUPPLY
15 CM.
1
2
3
4
TO TOEPLER PUMPS AND GAS ANALYSIS APPARATUS
CONDENSATION TRAPS

FIG 59.—All-glass ozonizer for hydrocarbon condensation with circulating system and low temperature collecting traps. Lind and Glockler, J. Am. Chem. Soc. 50, 1767 (1928).

same relations exist between the chemical reaction and the gaseous ionization both qualitatively and quantitatively. Since ionization in the ozonizer can neither be measured nor calculated, it was impossible to determine the ion yield. Hence the important bearing of alpha-ray yield.

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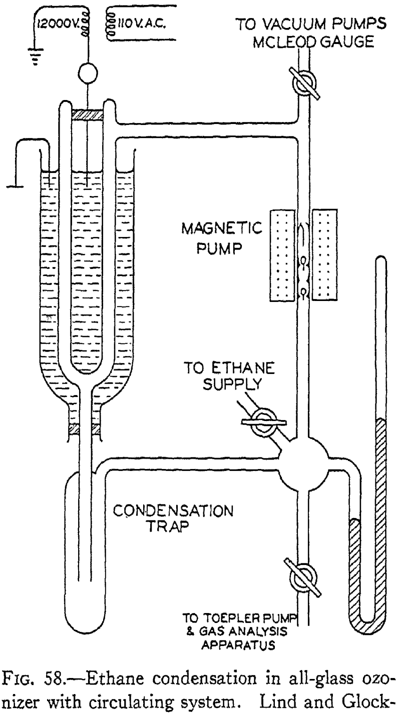

FIG. 58.—Ethane condensation in all-glass ozonizer with circulating system. Lind and Glockler, Trans. Am. Electrochem. Soc. 52, 37 (1927).

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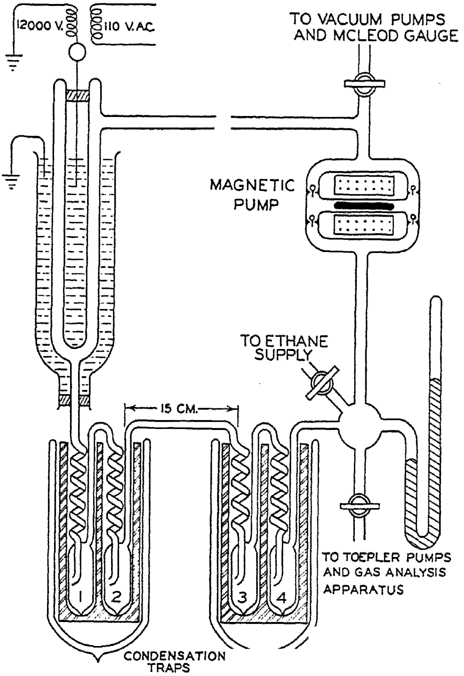
12000 V.
110 V.A.C.
TO VACUUM PUMPS AND MCLEOD GAUGE
MAGNETIC PUMP
TO ETHANE SUPPLY
15 CM.
TO TOEPLER PUMPS AND GAS ANALYSIS APPARATUS
1
2
3
4
CONDENSATION TRAPS

FIG 59.—All-glass ozonizer for hydrocarbon condensation with circulating system and low temperature collecting traps. Lind and Glockler, J. Am. Chem. Soc. 50, 1767 (1928).

It was found that, by raising the temperature of the ozonizer from 35° to 70° C., the average molecular weight of the liquid product was lowered from 467 to 105 (as determined by the freezing-point lowering in benzene). This rather remarkable difference for such a limited change in temperature was given the following interpretation. The liquid hydrocarbon forms from ethane gradually and deposits in small droplets on the ozonizer wall where it is in the direct path of electron bombardment, which causes further condensation to still heavier molecules accompanied by liberation of hydrogen – in this case, within the liquid. That this is so can be shown by lowering the gas pressure. The droplets then fairly effervesce in liberating gas from their interior. The length of time that a droplet is subjected to this secondary bombardment, that further raises its average molecular weight, depends on its rate of flow from the wall. Hence the liquid viscosity is a large factor which in turn is a function of the temperature.

Delayed condensation. The variation in the average molecular weight of the liquid material appears to depend on the length of time the earlier products remain in the discharge chamber subject to further ionization either in the gaseous or liquid state. Regulation of this factor by the two means already mentioned appears to afford satisfactory control of the degree of condensation. Some evidence of delayed condensation even in the gas phase has been discovered. The efficiency of condensation in long spiral traps at −50° to −58° C., has been surprisingly low. To prove that it was really a chemical condensation taking place in the gas phase and not merely a slow physical condensation in the trap or slow solution of low hydrocarbons in liquids already condensed, the following experiment was made. Four traps were placed at the same low temperature (−50° C.) with the connecting tubes at room temperature, spaced as shown in Fig. 59.

$$(1)\ \text{short} \rightarrow\ (2)\ \text{long} \rightarrow\ (3)\ \text{short} \rightarrow\ (4)$$

The order of liquid volume condensed was $(1) > (3) \gg (2) > (4)$, showing that the longer time elapsed in passage of gas from (2) to (3) allowed further polymerization at ordinary temperature. This delayed action can be attributed to the "open bonds" already referred to, which may of course play a role also in the delayed polymerization in liquids or solids, the slower there on account of slower diffusion. In this connection it is of interest to recall the condensation of methane to ethylene accomplished by Brewer (page 25) in glow discharge under conditions where the very first-step reaction product (C_2H_4) could be removed by the liquid-air-cooled wall from further condensation by the discharge.

Hydrocarbons, *continued.* In 1928 Pryanishnikov (75) used the ozonizer to produce a liquid from the dimethyl derivative of ethylene $(CH_3)_2C : CH_2$ which has the following properties: $d_4{}^{20} = 0.831$; $n_0{}^{20} = 1.4483$; average molecular weight 202; C 84.46%; H 14.60%; iodine number (Wijs) 156. Fractionation of the liquid brought out some interesting relations. The lighter fractions contain a higher ratio of H : C than the original C_nH_{2n}, which shows that there is some redistribution of hydrogen. The hydrogen-rich members remain in the fraction of low molecular weight on account of their smaller tendency to polymerize which has already been pointed out in discussing the alpha-ray results. Furthermore, Pryanishnikov points out that smaller radicals split off and then add together, which accounts for the low-boiling fractions 32–50° and 75–85° C. which have molecular weights in the range C_6 to C_7 hydrocarbons. Polymethylenes are present in much smaller quantity, though the 32–52° fraction probably contains $(Me_2CH)_2$ and $(Me_2C:)_2$. The 75–85° fraction probably contains $CH_2(CHMe_2)_2$, $C_3H_7 \cdot CMe_3$, Me_2CHCMe_3 and the corresponding pentenes as well.

The higher fractions are richer in unsaturates for the reason already given and also contain naphthenes. Probably no aromatic compounds are present. Pryanishnikov also found that the longer time favors the higher degree of polymerization. On the other hand, higher voltage causes faster reaction without changing the character of the product (presumably at the same temperature). The yield increases several fold on raising the voltage from 10 to 12 kv. Cyclopropane is polymerized only half as fast as propylene $(CH_3HC : CH_2)$. Heisig (76) found that in alpha-ray reactions the rate of the polymerization of cyclopropane is two-thirds that of propylene.

Fromandi (77) and Hock (78) studied the effect of silent discharge on decalin and on natural and artificial rubber dissolved in it. The primary effect on decalin is the splitting off of hydrogen; the secondary effect is the polymerization of the resulting unsaturate. Of course, there is no direct evidence that the process occurs thus rather than by initial clustering of ions and neutral molecules, followed by splitting out of hydrogen and stabilization of the condensation product when the ion cluster is neutralized by the returning electron. Ozonides are found in oxygen, and nitrogen is added in nitrogen atmosphere. Natural rubber dissolved in decalin isomerizes, and the iodine number, the viscosity, the softening point and the molecular weight decrease until cyclo rubber results, a powdery, very inert material. Synthetic isoprene rubber behaved similarly except that its molecular weight decreased at first.

Mignonac and de Saint-Aunay (79) circulated ethylene through a series of high-frequency ozonizers and condensed liquid polymers at $-60°$ C. By fractionation they isolated one-butene and one-hexene, which were identified by their ozonides. The polymerization of acetylene was the subject of a further communication (80) in which acetylene was reported to polymerize to the extent of 70% when electrodes were cooled to $-60°$ C. to a trimer which slowly underwent further polymerization. The product oxidized in air at room temperature. The trimer is a mixture of three constituents:

$$HC \vdots C{\cdot}CH(CH_3){\cdot}C \vdots CH; \qquad CH_2 : CH{\cdot}C \vdots C{\cdot}CH : CH_2;$$

$$CH \vdots C{\cdot}CH_2CH_2C \vdots CH$$

In 1929 Fischer and Peters (81) initiated a series of experiments on the treatment of methane in electrical discharge under various conditions, the principal object of which was to obtain the optimum yield of acetylene. Using a discharge tube with steel electrodes cooled by the incoming gases, methane and a mixture of methane and hydrogen were passed through at reduced pressures. At 50 mm. pressure, 1.3 kv-a., and 370 liters per hour they attained 8% acetylene, corresponding to 31 kv-a. per cubic meter. Other conditions were also used. The reaction consisted mainly of the dissociation of methane with partial conversion to acetylene. Orientative experiments of the same authors (82) at atmospheric pressure and temperatures from —185° to 750° C. showed little change of methane. At lower pressure (40 mm.) with a velocity of 367 liters per hour at room temperature and 5–7 kv. on electrodes 40 cm. apart in tubes of 35 to 60-mm. diameter and using gas initially containing 2.8% CO_2, 1.5% illuminants, 1.2% O_2, 52.3% H_2, 23.4% CH_4, 13.4% N_2 and no acetylene, they obtained 8.5% acetylene.

Lind and Glockler (72) investigated the reactions of methane, ethane, propane, *n*-butane and ethylene, respectively, on being passed at atmospheric pressure and various rates of flow through a series of twelve vertical glass tubes each having a central aluminum rod electrode and a trap below held at a suitable low temperature for the condensation of liquid products (Fig. 60). At 10–15 kv. all showed conversion to liquid in increasing amount in the order given above. The condensation is effected by the elimination of hydrogen and a smaller amount of methane. The slower rate for the lower members is attributable to two causes: the lower stopping power and ionization, and the greater amount of doubling or other condensation necessary to produce molecules large enough to condense as liquid. A very striking phenomenon was the distribution of liquid between successive traps all held at the same temperature in a common low-temperature bath. In all the gases, each succeeding tube numbered in the direction of gas flow, with rare exceptions, showed an amount of liquid product increasing regularly in the direction of flow until a tube with maximum yield was reached. Further tubes showed a gradual decrease in yield and the position of the tube with maximum amount of liquid product depends upon the rate of flow and is displaced downstream by a higher rate. (See Fig. 60).

The falling off in rate after the maximum is attributed to the accumulation of hydrogen and methane which dilute the gas and lower the stopping power for electrons. Although the increasing rate of liquefaction has not been wholly explained, it would seem to indicate the production of activated states which do not react immediately and which are increased in each successive tube until a maximum concentration is reached. Whether these states may be ions, free radicals or something else has not been determined. The alternative hypothesis that it may be the gradual accumulation of neutral larger molecules that have not yet attained a condensable size is not consistent with a clustered-ion hypothesis in the case of ethylene, which, from the alpha-ray results, we know has a yield of 5.5 molecules per ion pair, which would represent a molecular weight of 154 at once, well up in the liquid range. And yet ethylene showed the same increasing yield

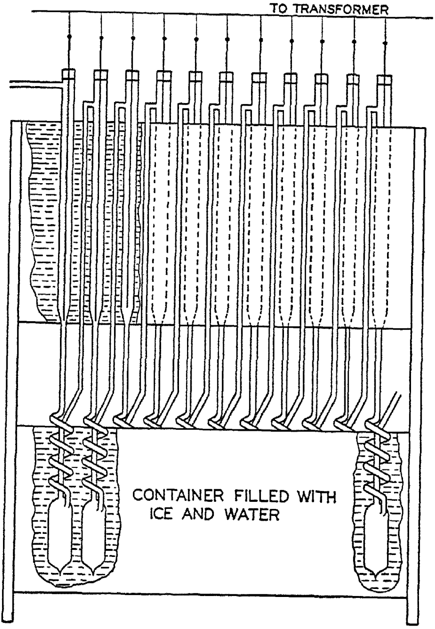

FIG. 60.—Multiple semi-corona. High-tension electrodes in parallel connection. Eleven discharge tubes in series gas flow. Lind and Glockler, J. Am. Chem. Soc. 51, 2811 (1929).

with successive tubes as did the saturated hydrocarbons, all of which have a yield of about 2 only.

Two types of solid product were also obtained: free carbon which built black carbon " trees " on the aluminum rod, and resinous solid hydrocarbons which deposited in very inert films on the walls which were very difficult to remove even with hot chromic acid mixture and sometimes had to be burned off with oxygen.

The liquids which collected in different traps from the same gas, and even from the different gases, had quite similar physical properties, as would be expected from the fact that they were removed from the field of further reaction at a common temperature as soon as they were large enough for such condensation. Such differences as they exhibited in index of refraction, density, color and viscosity, all of which increased or decreased in inverse proportion to the yield of liquid, were correlated with the time of exposure. The greater the yield of liquid per time, the smaller the hydrostatic head to cause flow and removal from the field of action, hence the higher the index of refraction, density, color and viscosity, as shown in Table 13 and Fig. 61.

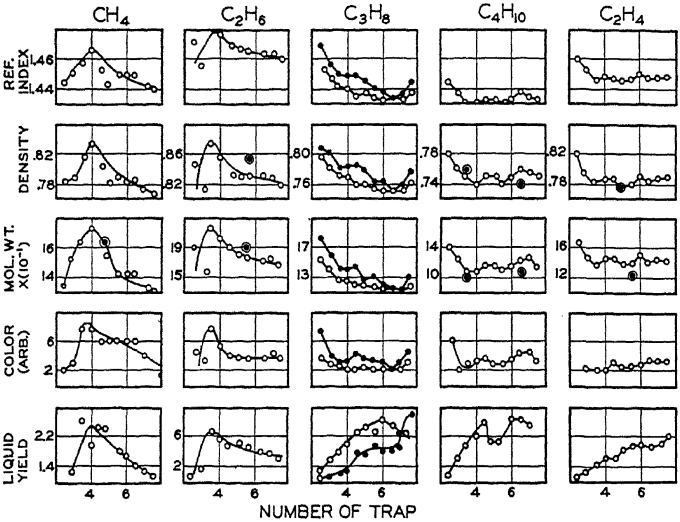

FIG. 61.—Properties of liquid condensates obtained from gaseous hydrocarbons in semi-corona discharge. Lind and Glockler, J. Am. Chem. Soc. 51, 2811 (1929).

Fractionation of liquid product. It has been seen that semi-corona discharge produces solid condensates when acting on gaseous hydro-

TABLE 13

Comparison of Experiments with Five Gaseous Hydrocarbons in the Eleven Semi-corona Apparatus

Central Aluminum Electrode ($\frac{1}{8}$-in. Diameter) in Pyrex Tubes (2.0-cm. Diam. and 1-mm. Wall Thickness)

S. C. Lind and G. Glockler, J. Am. Chem. Soc. 51, 2811 (1929)

	Methane	Ethane	Propane run 2	Butane	Ethylene
Flow, liters per hour	0.57	0.45	0.514	0.60	0.58
Temp. of trap, °C.	0	0	0	10	0
Time, days	5.1	1.5	10	5.7	12.4
Gas used (N.T.P.), liters	64.0	14.9	111	74.1	155
Gas used, grams	45.7	19.9	218	192	193
Volts (secondary)	18,000	18,000	18,000	18,000	18,000
Primary kw-hr	102.7	15.7	132.0	63.4	196.3
Yield of liquid, grams	18.25	9.74	63.42	71.10	40.10
Molecular weight of liquid produced	130–170	170–210	120–160	110–140	130–160
Density of liquid produced	0.78–0.83	0.81–0 87	0.75–0.82	0.74–0.78	0.78–0.82
$n^{20^\circ}_{\text{Sun}}$	1.44–1.46	1.46–1.48	1.42–1.47	1.43–1.45	1.45–1.46
Solid on glass wall, grams	4.4	0.1	63.64	(70.0)	78.6
Carbon on Al rod, grams	0.25	0.1	1.00	1.00	0.75
Conversion Efficiency (grams liquid)/(grams gas used), %	40	48	29	37	21
Grams (liquid + solid)/(grams gas used), %	50	48	58.5	73.5	61.4
Grams liquid/kw-hr	0.178	0.62	0.48	1.09	0.204
Grams (liquid + solid) per kw-hr	0.22	0.625	0.985	2.23	0.605

carbons, whereas such solid formation does not occur or is at least very much slower in an all-glass ozonizer of the Siemens type. Lind and Glockler (72) therefore arranged a bank of ozonizers as shown in Fig. 62, and studied the production of a large amount of liquid condensate from butane with the idea in mind to manufacture enough of the liquid material to be able to perform a fractional distillation on the product, which was obviously a mixture. They produced 832.8 grams of liquid hydrocarbon from 5420 grams of butane. The initial butane is, of course, soluble in the resulting liquid mixture, and 147 grams of butane were recovered from the product. Hence the efficiency of conversion was 13% by weight.

The ozonizers were connected in parallel with 12,000 volts on the high-tension terminals. The butane gas was used at a rate of flow of 3.46 liters (25° C., 1 atm.) per hour, and the tubes were arranged in parallel as to gas flow. On account of the possibility of breakdown and fires resulting therefrom it was necessary to watch the apparatus continually during the 659.2 hours of the run. The temperature of the ozonizers was about 50° C. owing to the electrical energy consumed (356 kw-hr.) since the twelve ozonizers were protected by asbestos boards (not shown in Fig. 62); the performance of the apparatus was followed by noting daily the amounts, color and index of refraction of the liquid product. Its average index of refraction was 1.4600, and its average molecular weight in benzene by the freezing-point method was found to be 178. The color on an arbitrary scale of the Union Oil Co. colorimeter was 2.75 scale readings. The exit gases were not analyzed, since the primary object of the research was the production and fractionation of the liquid condensate.

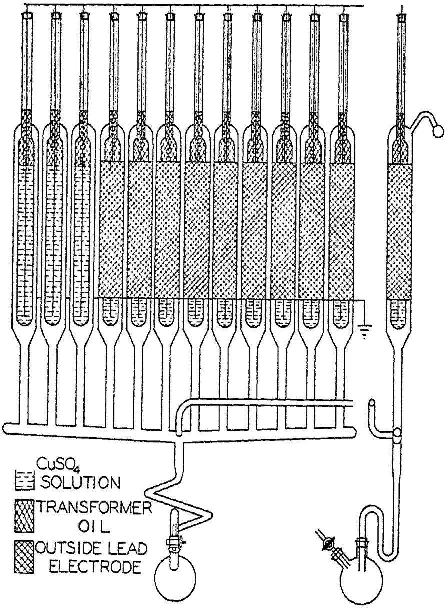

Fig. 62.—Multiple all-glass ozonizers for liquid hydrocarbon synthesis from butane. Lind and Glockler, J. Am. Chem. Soc. 51, 3655 (1929).

The total product was separated into three main fractions by means of a chain still of the type used by Washburn (83) in a study of the composition of naturally occurring petroleum. The primary step in the separation process is shown in detail in Table 14. The first distillation was carried out at low pressure, using liquid-air traps to avoid loss.

TABLE 14

FRACTIONS OBTAINED FROM LIQUID CONDENSATE PRODUCED IN OZONIZER FROM GASEOUS BUTANE

S. C. Lind and G. Glockler, J. Am. Chem. Soc. **51**, 3655 (1929)

	Density	Weight, Grams	Boiling point range, °C.	Index of refraction
I. Light fraction (in liquid air trap).........	0.740	335	0°–160° (740 mm.)	1.3713–1.4334
II. Middle fraction (condensed at room temperature)..........	0.795	93	78°–112° (5 mm.)	1.4386–1.4558
III. Heavy fraction (remainder as residue)	0.872	405	230°–· · · (10^{-4} mm.)	1.4855
	0.804	833		

The middle fraction II. The fractions noted in Table 14 are still complex mixtures of liquid hydrocarbons, and they were in turn subjected to further fractional distillation. The middle fraction II was thus separated (at 5-mm. pressure) into five subfractions boiling between 90 and 98° C. with a large residue of 38 grams. These subfractions were again distilled at low pressure in a small still into fourteen other fractions. The range of boiling points widened from 78 to 112° C. The amounts of the fractions were now rather small, and no further attempts were made to separate the " middle fraction II."

The heavy fraction III. This material was the residue which remained in the distilling flask after the first distillation. It was very viscous and had an average index of refraction of 1.4855. Beyond the fact that this portion is still a mixture, nothing has been found out about it. It was possible to distil from this heavy oil a much lighter colored yellow oil at 230° C. in a nickel-shot bath at very low pressure (10^{-4} mm.). This material may have been produced by thermal cracking.

The light fraction I. This low-boiling section is the part caught in the liquid-air trap. It contained dissolved butane. This gas was removed and its boiling point determined. The total amount of butane (147 grams) was distilled at 0° C. with exception of a few cubic centimeters which remained as a residue and which must represent slightly higher hydrocarbons. The next fraction which resulted from the distillation was separated into eleven subfractions by making cuts at every 10° C. The distillation curve is given in Fig. 63. The largest fraction (I-6; 33 grams) distilled in the interval between 110 and 120° C., and it was therefore redistilled into five subfractions boiling between 105 and 117° C. (Table 15.)

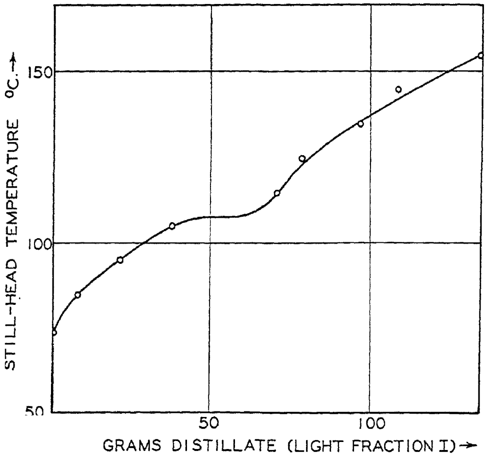

FIG. 63.—Distillation of the light fraction of liquid hydrocarbons synthesized from butane by silent discharge. Lind and Glockler, J. Am. Chem. Soc. 51, 3655 (1929).

Identification of fraction I-6-2. On comparing the boiling point of this fraction and its index of refraction with the properties of known hydrocarbons (International Critical Tables) it was found that two octanes fit closest in these properties. They are 2-4-dimethylhexane and 2-methyl-3-ethylpentane. Several constants of the unknown hydrocarbon were therefore determined, such as density, carbon-hydrogen ratio, molecular weight by the freezing-point method in benzene and halogenation number. At the same time these methods were checked on a sample of pure heptane. The combustions were carried out on 0.200-gram samples in an enclosed system (66) since ordinary methods of carbon-hydrogen combustion yielded low results

TABLE 15

FRACTIONATION OF SUBFRACTION I-6 INTO FIVE SUB-SUBFRACTIONS

(Barometer 744.2.) Part of Liquid Product from Butane Condensation in Ozonizer. S. C. Lind and G. Glockler, J. Am. Chem. Soc. **51**, 3655 (1929)

Number of fraction	Temperature of stillhead, °C.	Index of refraction, $n_{\text{sun}}^{20°}$	Distillate, grams
I-6-1	105.0–110.0	1.4004	0.5
I-6-2	110.0–113.0	1.4021	8.0
I-6-3	113.0–115.0	1.4029	6.0
I-6-4	115.0–117.0	1.4036	2.0
I-6-5	117.0	1.4118	10.0
			26.5

owing to difficulty in burning the unknown hydrocarbon. Its properties are shown in Table 16. The unknown I-6-2 is not a saturated hydrocarbon but is most likely a mixture of octanes and octylenes. Further fractionation was not carried out because the separation of octanes and octylenes had not been completely accomplished even with ordinary hydrocarbon materials.

The fact that eight carbon atoms appear in the largest fraction of the condensate seems understandable quite simply on the basis of the cluster theory of ionic gas reactions (I, 7). On this basis the changes leading to condensation by doubling are as follows:

$$C_4H_{10} \rightarrow C_4H_{10}^+ + E^- \text{ (ionization)}$$

$$C_4H_{10}^+ + C_4H_{10} \rightarrow [C_4H_{10} \cdot C_4H_{10}]^+ \text{ (clustering)}$$

$$[C_4H_{10}]_2^+ + E^- \rightarrow C_8H_{18} + H_2 \text{ (neutralization and rearrangement of the cluster)}$$

$$[C_4H_{10}]_2^+ + E^- \qquad\qquad 2H_2$$

Since any butane ions formed would meet with neutral butane molecules most frequently because of their greater concentration, it is to be expected that octanes would form relatively in greatest amount. Of course, other possible hydrocarbons can be built by continued and successive actions of the type referred to. Since decomposition would also take place it is readily understood that probably all possible combinations of radicals occur in such a manner as to produce a most complex mixture of hydrocarbons. The octylenes found can be

TABLE 16

PROPERTIES OF PURE HEPTANE, THE UNKNOWN HYDROCARBON "I–2–6" AND TWO OCTANES

"I–2–6" is Part of the Liquid Product Obtained from Butane Condensation in the Ozonizer. S. C. Lind and G. Glockler, J. Am. Chem. Soc. **51**, 3655 (1929)

Property	Heptane		Octanes	
	Known from I.C. Tables	As determined	2-4-dimethylhexane and 2-methyl-3-ethylpentane (I.C. Tables)	Unknown I-6-2
Boiling point	98.0° C.	97–98° C.	110.0–114.0° C.	110.0–113.0° C.
Density	0.684	0.681	0.708	0.708
Index of refraction	1.3850	1.3855	1.4016–26	1.4021
% Carbon	83.90	83.79	84.11	84.55
% Hydrogen	16.10	16.21	15.89	15.45
Molecular weight:				
by freezing point	100.12	102.0	114.1	114.7
by combustion	....	......	....	113.5
by halogenation	....	......	....	113.7
Empirical formula (by combustion)	C_7H_{16}		C_8H_{18}	$C_8H_{17.4}$
Unsaturation:				
(by combustion)	....	......	....	30.0%
(by halogenation)	....	......	....	22.5%

thought to be formed by splitting off two hydrogen molecules upon reaction and rearrangement.

Hydrocarbons, *continued.* Brewer and Kueck (I, 17) studied the reaction of methane in glow discharge

$$2CH_4 \rightarrow 2H_2 + C_2H_4$$

They concluded that two molecules react per ion pair

$$CH_4^+ + CH_4 + E^- \rightarrow 2H_2 + C_2H_4$$

Peters (84) has considered the thermodynamic conditions of the reaction

$$2CH_4 \rightarrow C_2H_2 + 3H_2$$

He calculated that it may start thermally at 750° C. and that it is possible in the arc and in the low-pressure arc.

In actual experiments in passing methane through the arc, Frolich and his collaborators (85) found that much free carbon is formed, but that it may be suppressed by excess of hydrogen. Two moles of methane in a single passage gave one mole of hydrogen and 50% of acetylene in the gaseous mixture corresponding to a yield of 68%.

Stanley and Nash (86) passed methane through spark discharge in a 1-liter glass sphere. The free carbon which formed was dislodged by a scraper operated by hand. Gaseous, liquid and solid hydrocarbons were obtained. The gas contained acetylene up to 15% and hydrogen up to 65%. Excess hydrogen, as in the arc, repressed the liberation of carbon but gave some ethylene and ethane. The liquid was light, oily, consisting of polymers of unsaturated hydrocarbons and containing a small amount of benzene. The first step of the reaction yields the CH radical. Diacetylene is formed by the reaction

$$2C_2H_2 \rightarrow HC \vdots C{\cdot}C \vdots CH + H_2$$

Gold, platinum, iron or aluminum were used as electrodes without making a difference in the results.

Fujio (87) passed methane, ethane and ethylene, respectively, through the spark between spherical electrodes at 8–47 kv. Methane yielded 5 volumes of hydrogen to 1 of acetylene. Ethane yielded hydrogen, acetylene, methane and ethylene, while ethylene gave 2 volumes of hydrogen to 1 of acetylene and a little methane.

Harkins and Gans (88) subjected benzene vapor at a pressure of less than 0.1 mm. to electrodeless discharge from a source of 25,000 volts with a condenser of 0.02 μf. and a frequency of 1000 kc. Spectroscopic observation revealed bands characteristic of C_2 and CH molecules and lines of C^+ and H atoms. A solid reddish brown polymer $(CH)_x$ is formed. Many thousand liters of benzene at this low pressure were passed into the vessel and polymerized without building up any pressure of hydrogen.

Later Harkins and Gans (VI, 73) used the same method for further experiments with benzene and extended them to acetylene, naphthalene, and toluene. Again spectral evidence was obtained for CH, C_2, C, H and C^+, all of which are very active and unite rapidly to form brown or black inert solids insoluble in water and probably having high molecular weight. Toluene gave very little solid. Aniline and phenol were also examined. (See also Chapter III, page 62, and Chapter VI, page 113.)

Austin (89) also employing electrodeless discharge confirmed the results of Harkins and Gans, using benzene, pentane, 2-2-4-trimethylpentane, acetylene, ethyl chloride and cyclohexane. They also obtained large amounts of a reddish brown solid deposit, except with cyclohexane, from which very little solid was obtained.

Karapetoff, Trebler and Linder (90) subjecting the vapors of various hydrocarbons to electronic bombardment obtained polymerization and condensation products and some gases, chiefly hydrogen. Various tubes containing a filament, grid and plate (Fig. 50) were tried, and the thermal decomposition due to the hot filament was corrected for. The investigations seemed to indicate that aromatic and unsaturated compounds give off less gas than the corresponding saturated substances (122). (See also page 26.)

The same investigators (122) also studied *n*-decane and *m*-xylene, a paraffin and an aromatic hydrocarbon under the influence of a high-frequency discharge (1 kw., 1270 kc.). An intense discharge took place in the hydrocarbon vapors, and wax formation was observed. The *n*-decane gave over twice as much gas as the *m*-xylene, but only about one-seventh the amount of solid was obtained (page 323).

Austin and Black (91) exposed the vapors of benzenoidhydrocarbons to Tesla discharge in a glass Dewar flask provided with inlet and outlet to a vacuum pump. The reaction took place at 0.1 to 1.0 mm. pressure and 40 to 50° C. Two types of products were obtained. One was a shellaclike inert deposit on the walls which was insoluble in the ordinary organic solvents and in alkali and acid. Analysis for carbon and hydrogen showed a marked deficiency from 100% (20% or more) in the products from benzene (C 73.38%; H 4.77%); from toluene (C 79.16%; H 5.90%) and from *p*-xylene (C 77.14%; H 6.52%), which they attribute to the addition of oxygen from water vapor in the discharge. However, no statement is made of the time elapsing before analysis during which the products may have absorbed oxygen from the atmosphere, nor what the opportunities may have been for oxygen to diffuse back from the pump against the low-pressure vapor stream.

The second type of product obtained by Austin and Black consisted of relatively simple molecules condensing in well-defined crystals, as diphenyl from benzene and dibenzyl from toluene. The following primary reactions are assumed to take place, which may be succeeded by further polymerization or condensation.

$$2C_6H_6 \rightarrow C_6H_5 \cdot C_6H_5 + H_2$$

$$2CH_3 \cdot C_6H_5 \rightarrow C_6H_5 \cdot CH_2CH_2 \cdot C_6H_5 + H_2$$

$$2CH_3 \cdot C_6H_5 \rightarrow CH_3 \cdot C_6H_4 \cdot C_6H_4 \cdot CH_3 + H_2$$

$$2CH_3 \cdot C_6H_4 \cdot CH_3 \rightarrow CH_3 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot CH_3 \qquad H_2$$

$$4C_6H_5Cl \rightarrow 2C_6H_6 + 2Cl_2 -$$

Comparison of alpha-ray and ozonizer reactions. Lind and Glockler (72) showed that in methane, ethane, propane, butane and ethylene the alpha-ray and electrical condensations are similar with respect to their principal characteristics, including: (1) the relative velocity of reaction, (2) the relative amount of hydrogen liberated, (3) the relative quantities of hydrogen and methane liberated, (4) the percentage conversion to liquid, and (5) the average composition of liquid by analysis of hydrogen and carbon. Hence a similar mechanism was assumed in both cases, and a complete theory was based on interaction between gas ions as primary agents and neutral molecules. An important part of the theory is the assumption that the larger hydrocarbon molecules are readily ionized by electron exchange in collision of the second kind with smaller ions, on account of the lower ionization potential of the larger molecules. The experimental details may be seen from Figs. 64 to 66 and Table 17.

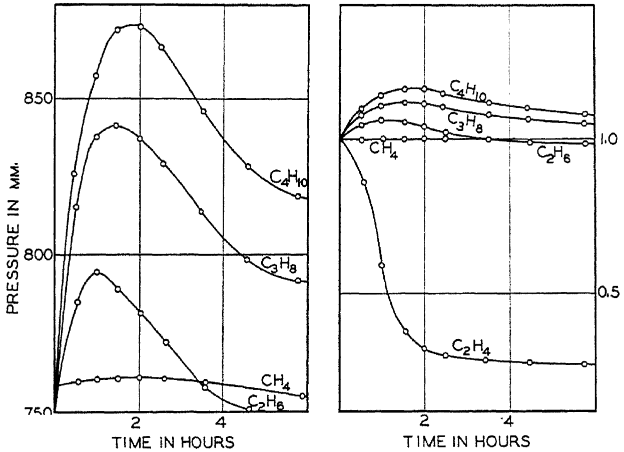

FIG. 64.—Pressure changes during condensation of hydrocarbons in an ozonizer. Lind and Glockler, J. Am. Chem. Soc. 52, 4450 (1930).

Lind, Marks and Glockler (IV, 50) projected high-speed cathode rays (125,000 volts) from a Slack-Lenard type of tube with thin glass window through a flat cell also provided with a thin glass window. The relative reactivity of methane, ethane, propane and butane was found to increase in the order given, which is the same as for alpha particles. This was regarded as indicating that their relative stopping powers and specific ionizations are the same for electrons as those well known for alpha particles. (See also Chapter IV, page 85.)

M/N ratios for ozonizer reactions. However, the evidence offered so far for the similarity of alpha ray and ozonizer condensations of hydrocarbons has been only semi-quantitative in nature. Strong support would be furnished if it were possible to determine the ratio of molecules reacting (*M*) to ion pairs (*N*) formed in an ozonizer, as has been done for alpha-ray reactions. Since the ionization cannot be determined in electrical discharge, absolute values of these *M*/*N* ratios cannot be obtained but relative values may be established as has been

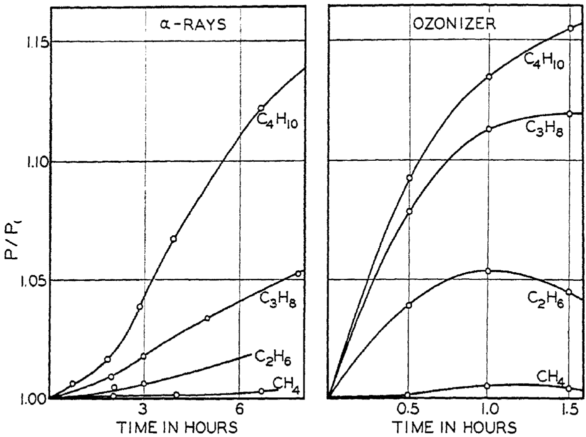

FIG. 65.—Comparison of pressure changes in the alpha-ray and ozonizer condensations of saturated hydrocarbons. Lind and Glockler, J. Am. Chem. Soc. 52, 4450 (1930).

done by Lind and Schultze (92). They made a very careful study of the condensation of methane, ethane, ethylene and acetylene in a circulating system containing an ozonizer (Fig. 58) and found that short runs of 20-min. duration were very reproducible and that a 1-hour run was too long because the acetylene would become somewhat depleted under the conditions of their experiments. Fig. 67 shows the pressure drop. These runs can be reproduced satisfactorily if sufficient care is exercised in maintaining proper conditions. An interesting effect was observed with acetylene. The solid product (cuprene) would deposit on the glass walls of the ozonizer in the shape of a closely adhering film which had a decided effect on the reaction velocity. It served as a

TABLE 17

Condensation of Five Hydrocarbons in the Electrical Discharge (Ozonizer) and by Means of Alpha Rays

S. C. Lind and G. Glockler, J. Am. Chem. Soc. **52**, 4450 (1930)

	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_2H_4
(1) Pressure changes					
Final pressure/initial pressure (ozonizer)	1.00	0.99	1.05	1.07	0.29
Final volume/hydrocarbon used (ozonizer)	1.00	0.99	1.06	1.07	.27
Maximum pressure/initial pressure (ozonizer)	1.03	1.07	1.14	1.16	....
Final volume/volume hydrocarbon used (alpha rays)	1.01	1.09	1.14	1.13	.32
(2) Free hydrogen					
$-(\Delta\text{hydrocarbon}/\Delta H_2)$ (ozonizer)	1.17	1.37	1.44	1.50	4.70
$-(\Delta\text{hydrocarbon}/\Delta H_2)$ (alpha rays)	1.32	1.31	1.54	1.44	4.18
(3) Hydrogen-methane ratio					
$\Delta H_2/\Delta(H_2 + CH_4)$ (ozonizer)	....	0.77	0.80	0.80	0.86
$\Delta H_2/\Delta(H_2 + CH_4)$ (alpha rays)	....	.83	.79	.84	.90
(4) Liquid conversion					
Per cent (ozonizer)	54	77	74	77	93
Per cent (alpha rays)	30	56	52	71	96
(5) Liquid composition					
Empirical formula (ozonizer)	C_nH_{2n}	C_nH_{2n}	C_nH_{2n}	C_nH_{2n}	$C_nH_{1.7n}$
Empirical formula (alpha rays)	C_nH_{2n}	$C_nH_{1.9n}$	$C_nH_{1.8n}$	$C_nH_{1.9n}$	$C_nH_{1.7n}$
(6) Hydrocarbon reacted					
Per cent (ozonizer)	73	88	93	95	100
Per cent (alpha rays)	18	27	45	68	92

All these factors are quite similar for both types of condensation, and it is argued that they must be caused by the same mechanism.

negative catalyst for the condensation. Whereas in a given run 81% of the acetylene had reacted in 20 min. with the glass wall clean at the beginning of the experiments, it was found that, in a second experiment with the cuprene present from the first run, only 22% of the gas condensed in the same time. No progressive decrease of reaction velocity was detected when the skins of several runs, one following the other, were left in the ozonizer. The effect is apparently a catalytic one and not due to high stopping power or a high resistance of the wall skin. Nor would the thin film of cuprene increase the dielectric materially. It is conceivable that the very smooth surface offered by the deposit

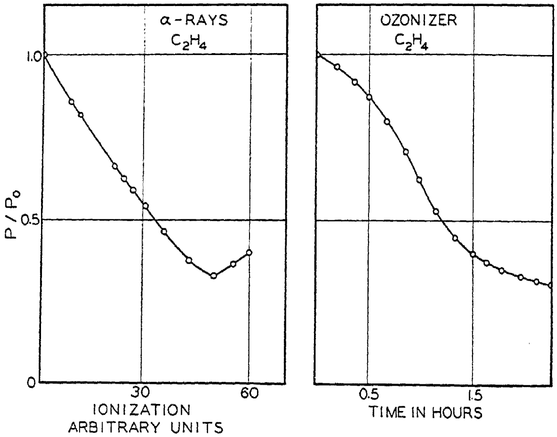

FIG. 66.—Comparison of pressure changes in the alpha-ray and ozonizer condensations of ethylene. Lind and Glockler, J. Am. Chem. Soc. 52, 4450 (1930).

does not form as many points of discharge for current passage as does a glass surface, and hence less current passed through the gas and less ionization is produced with a consequent decrease in condensation rate.

Following a suggestion made by Lind (93), Lind and Schultze (92) adopted the view that the reaction rate in electrical discharge is proportional not only to the M/N ratio of the alpha-ray reaction but also depends on the molecular ionization (ks). This latter quantity gives the relative ionization of various gases and must be taken into account in order to arrive at a proper evaluation of the ionization in electrical discharge. This situation may be illustrated in simple terms as follows: Consider two reactions, 1 and 2, being activated by electrical

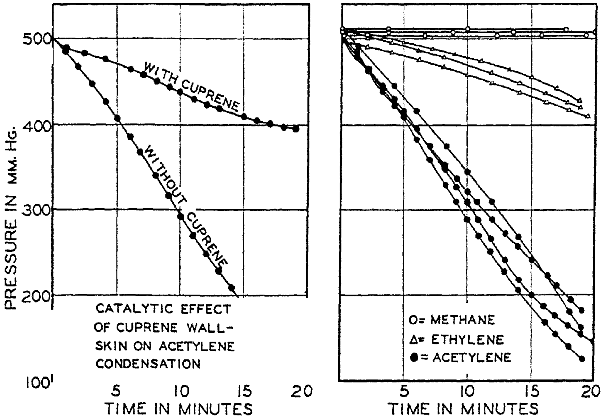

FIG. 67.—Pressure drop in hydrocarbon condensation. Wall skin effect in acetylene and 20-minute runs under comparable conditions in methane, ethylene, and acetylene. Lind and Schultze, Trans. Am. Electrochem. Soc. 59, 165 (1931).

discharge and by alpha rays. The corresponding M/N ratios are for the ozonizer reaction

$$\frac{M_e'}{N_e'} = R_e' \quad \text{and} \quad \frac{M_e''}{N_e''} = R'' \tag{1}$$

Let then

$$\frac{M_e'}{N_e'} \cdot \frac{N_e''}{M_e''} = \frac{R_e'}{R_e''} = R_e \tag{2}$$

and for the alpha-ray reaction

$$\frac{M_a'}{N_a'} \cdot \frac{N_a''}{M_a''} = \frac{R_a'}{R_a''} = R_a \tag{3}$$

But if the radon and ozonizer reactions both proceed by the same mechanism then

$$\mathrm{R}_e = R_a \tag{4}$$

and from (2)

$$\frac{M_e'}{M_e''} \cdot \frac{N_e''}{N_e'} = R_e = R$$

Using Lind's suggestion that

$$\frac{N_e'}{N_e''} \qquad \overline{ks''} \tag{5}$$

we find

$$\frac{M_e'}{M_e''} = \frac{R_a'}{R_a''} \cdot \frac{\overline{\overline{ks'}}}{\overline{\overline{ks''}}} \tag{6}$$

or "the relative number of molecules reacting in two different cases is proportional to the product of their alpha ray M/N ratios and the molecular ionization." Lind and Schultze tested this proposition on methane, ethane, ethylene and acetylene.

It is found that the values of M_e (percentage of hydrocarbon reacted in 20 min. in an ozonizer) vary as follows: methane : ethane : ethylene : acetylene as 7.9 : 17.0 : 39.6 : 75.5 or as 2.0 : 4.3 : 9.9 : 19.1. The M/N ratios obtained from alpha-ray work vary as 2.0 : 2.0 : 5.0 : 19.8. It is seen that ethane and ethylene do not follow the same trend. The molecular ionizations of these gases have the relation 1.0 : 2.0 : 1.7 : 1.4. If this correction ks is applied to the above-mentioned M/N values the following relation is obtained: The products $M/N \cdot ks$ vary then as 2.0 : 4.0 : 8.5 : 27.7, and the expected trend is found with only acetylene showing an exceptional behavior. Evidently the ks correction must be refined to obtain a completely satisfactory situation.

Various factors in hydrocarbon condensation. Although the results discussed so far tend to establish the thesis that alpha-ray condensation and ozonizer reaction have a great deal in common and hence most likely occur by the same detailed mechanism, still there has been no clear-cut experimental proof in favor of any particular mechanism, be it ionic, photochemical or by means of radicals or even atoms. The question is not settled, and very probably it will not be decided until we have more information regarding the electrical discharge. Further experiments are needed in order to establish more detailed facts regarding these condensations. Lind and Schultze (94) have attempted to contribute towards this end by studying ozonizer reactions at lower pressures and during shorter periods. In the case of methane the total amount of gas reacted in a given time rapidly increases with decrease in pressure, as is to be expected from the increased ionization at lower pressures. Similarly liquid conversion is better at low pressures. Small amounts of unsaturated compounds are found at pressures of 200 mm. Hg. At lower pressures they are probably reduced by the large amounts of hydrogen formed, since the percentage of free hydrogen rapidly increases with the pressure. The time of reaction has the following influence on the condensations studied. The action on methane is proportional to the time within the first hour. The absolute amounts of higher hydrocarbons in the gas phase do not change between a 20-min. and a 6-hour run. In the earlier part of the reaction, less liquid is produced than later; the steady state has not yet been reached. There seems to exist an induction period during which an equilibrium state is built up whereby the same amounts of each hydrocarbon are decomposed as are formed. Later the rate of formation of liquid and of hydrogen reaches a constant value. Finally a slow decomposition of the liquid product is the only essential change taking place. Similar facts have been established for ethylene and acetylene condensations. In the latter case it has been found that a certain amount of hydrogenation takes place which is not observed with alpha-ray activation. The facts cited will have to be considered in a program intended to establish the complete and detailed mechanism of hydrocarbon reaction in electrical discharge.

Hydrocarbons, *continued.* Peters and Pranschke (95) experimented with the production of acetylene from coke-oven gas. They studied the effect of varying the rate of flow, the concentration of methane, tube design, voltage, current density, electrode design and position. The energy required was reduced to 12 kw-hr. per cubic meter of acetylene. The efficiency of utilization of electrical energy was estimated as 38%. For optimum yield the gas contained 25% of methane, flowed at the rate of 100 liters per hour and, in addition to acetylene, produced 5% of ethylene.

The work on the formation of acetylene and ethylene by various kinds of electrical discharge in methane was fully reviewed by Peters (96) in 1931. Egloff, Lowry and Schaad (97) in 1932 collected and critically reviewed the literature on the decomposition and polymerization of acetylene and its homologues by heat, light, electricity and chemical action.

Davis (98, 122) treated benzene vapor at 300° C. in an ozonizer actuated by a Tesla coil and found that the main reaction leads to the formation of a resinous product which contains hydrogen and carbon atoms in the ratio of 6 to 4. The best solvent for the resin is chloroform. Diphenyl formation is the next important reaction. A small amount of *p*-diphenylbenzene was also isolated. Hydrogen that should have appeared at the time of the production of the resin and diphenyl was not found in the gas phase. It was probably used up in some secondary reactions. Linder and Davis (122) found benzene vapor to undergo the following three reactions in the ozonizer at 37,000 volts (60 cycles): (1) formation of diphenyl with the evolution of hydrogen; (2) breaking up of the molecule into unsaturated gaseous product; and (3) polymerization. These types of reaction were found to be in agreement with mass-spectrograph findings (XVII, 71).

Linder and Davis (I, 22) made an extended investigation of the gases liberated from various homologous series of hydrocarbons in glow discharge. They established that the rate of evolution increases with the molecular weight of members within a series and with the decentralization in isomeric hydrocarbons. The amount of insoluble residue increases with the ratio of carbon to hydrogen. Rates of gas evolution were determined for fifty-seven hydrocarbons, for forty-seven of which gas analyses are given.

Montagne (99) used the condensed spark to study the reaction: $2CH_4 \rightleftharpoons C_2H_2 + 3H_2$ in methane at pressure of 1 to 11 mm. About 75% of conversion takes place accompanied by partial decomposition of methane and polymerization of the acetylene. The reaction is accelerated and the yield increased by increasing the capacity of the condenser. Lefebvre (100) obtained similar results.

Meneghini and Sorgato (101) by subjecting a mixture of amylene vapor and hydrogen to silent discharge transformed 85% into liquid products in which molecules containing five and ten atoms of carbon, respectively, predominated. The gaseous products were mainly acetylenic hydrocarbons. Amylene alone or with nitrogen failed to give liquid. In corona discharge the reaction was much smaller and free carbon was separated. The reaction was interpreted as showing that hydrogen acts both as a hydrogenating and dehydrogenating reagent. This reminds one of the attempt to hydrogenate ethylene by alpha rays (I, 7), where it was found that condensation predominates accompanied by the liberation of much more hydrogen than is used in the slight formation of ethane. One of the principal roles of hydrogen in promoting reaction in electrical discharge is probably to be seen in its furnishing a ready medium for passage of current owing to its lower stopping power at a given pressure.

Meneghini and Sorgato (101) also found the same tendency noted by Lind and Glockler (72) for molecules to double, yielding liquid in the range 140–146 molecular weight from amylene. In addition complex reactions take place including bond transposition, cyclization, polymerization, cleavage and rearrangement. Simultaneous ionization and excitation are suggested as being responsible for the complexity.

Vernazza and Stratta (102) found the rate of formation of acetylene from ethylene in silent discharge to be independent of the rate of gas flow if the reaction products were not removed as formed. The presence of hydrogen caused the formation of saturated hydrocarbons. Stratta and Vernazza (103) found that the polymerization of acetylene in silent discharge in the presence of nitrogen or argon up to 20% is proportional to the amount of acetylene. (This has been confirmed by Lind and Schultze in unpublished experiments.) Stratta and Vernazza found the rate of polymerization of acetylene in the presence of hydrogen to be more rapid at the start but to slow down to normal as the reaction proceeds. The rate of formation of acetylene from ethylene decreases rapidly with decrease in the concentration of ethylene. The hydrogen formed reacts at once with the unsaturated hydrocarbons.

Szukiewicz (104) confirmed the results of Mignonac and de Saint-Aunay (105) in the condensation of ethylene in silent discharge. At low power input as much as 60% of the product was butylene. A maximum of 18% of acetylene was obtained under certain conditions. Under other conditions 1-3-butadiene was obtained.

Using Berthelot's apparatus, Volmar and Hirtz (106) found that hydrogen at low pressure reacts with charcoal coated with mercury to form hydrocarbons with yields as high as 7% at 8000 volts. HgH_3 was suggested as the active intermediate.

In 1935 Gobert (107) showed that the electric arc submerged in liquid hydrocarbons produces a gas containing 35–40% acetylene, 35–40% hydrogen, 5–10% ethylene and derivatives, and small amounts of methane and nitrogen. One cubic meter of gas containing 40% of acetylene was produced from 800 grams of oil with an expenditure of 3.5 kw-hr.

In 1933 de Saint-Aunay (108) reviewed the nature of the chemical reactions which hydrocarbons undergo in electrical discharge and claimed that types of reaction such as polymerization, dehydrogenation or decomposition may be made dominant by controlling the conditions. Various reactions in these several classes are cited as examples.

In 1934 the literature (including patents) of the action of silent discharge on gaseous hydrocarbons was reviewed by Nash, Howard and Hall (109).

Rubanovskiĭ (110) has shown in glow discharge in butadiene from 10^{-3} to 10^{-1} mm. that decomposition alone occurs. Above 10^{-1} mm. polymerization predominates. In a mixture of butadiene and hydrogen polymerization also occurs which was attributed to shock impacts of atomic hydrogen. An induction period was observed in all cases of polymerization. Acceleration of the rate by oxygen, by argon and by increasing the size of the vessel were all regarded as evidence of chain mechanism.

Kobozev, Vasil'ev and Gal'braikh (111) varied the electrode material in studying the conversion of methane into acetylene in glow discharge. Between aluminum, gold, iron, zinc and lead electrodes the conversion of methane to acetylene and ethylene did not exceed 1.5%.

Mercury electrodes gave 5.2% and as much as 14% conversion when heated. The effect is due to mercury vapor in the discharge. Sodium (2%) amalgam reduced the conversion below one per cent.

Balandin, Eidus and Zalogin (112) polymerized ethylene in high-frequency (7.8×10^5) discharge obtaining a viscous oil, free carbon and hydrogen. In a closed system ethylene was converted in 10 hours into 67% hydrogen and 20% saturated hydrocarbons of which 5.3% was methane. In a circulation system butadiene reaches 6.4% of the original ethylene. Induction period and sensitivity to traces of water vapor point to a chain mechanism.

Christen (113) found that heptane in alternating current from 300 to 600 volts between nickel electrodes gives hydrogen and a yellowish brown condensate of low vapor pressure which absorbs oxygen slowly.

Mund and Jungers (114) measured the yield in the polymerization of acetylene when brought about by beta rays from radium. They found that 26 molecules of acetylene polymerized per ion pair. They attribute this higher yield, compared with 20 for alpha particles, to a higher clustering efficiency owing to the longer life or slower rate of recombination of the ion pairs when produced by beta rays.

Volmar and Hirtz (115) examined the conditions for hydrogenation of acetylene and ethylene in silent discharge. They found that hydrogenation occurs at those pressures and in those mixtures in which polymerization and dissociation are at a minimum. Low pressure favors hydrogenation. The optimum mixtures were $1C_2H_2$ to $4H_2$ and $1C_2H_4$ to $8H_2$.

Lind and Schultze (94) studied a number of factors involved in the reactions of simple hydrocarbon gases in ozonizer discharge in a circulating system. For methane they showed that the percentage of reaction completed, measured either as liquid formed or total gas reacted, increases rapidly as the initial pressure is reduced. This is due to the greater ease of conduction and ionization at lower pressure, which has already been mentioned. The liberation of hydrogen also increases at reduced pressure. In methane it was also shown that the rate of reaction is proportional to the time for at least the first hour except in the very early stages of the reaction when it is slower; also in the latter stages when hydrogen accumulates in large amounts it is retarded. An induction period was observed for about 25 min. By pumping out the gaseous products and allowing discharge to continue, it was shown that the last stage of the reaction consists in the slow evolution of gas from the liquid product, probably accompanied by further condensation.

In the case of ethylene the condensation is so rapid that it was difficult to determine whether an induction period exists, but by analogy with the flow experiments in semi-corona it appears probable.

The experiments with acetylene did not indicate that the hydrogen evolution is from the solid polymer already formed, as in alpha-ray polymerization, for the amount of hydrogen evolved in the first 20 min. was not less than proportional to that in the first hour.

The hydrogenation of acetylene in a 1 : 1 mixture with hydrogen was shown to occur though not so rapidly as polymerization. Of the 36% of hydrogen that reacted when 99% of acetylene had condensed, some went to form methane, ethane and ethylene while the larger proportion went into the solid and liquid products.

Becker (116) examined the effect of high-voltage discharge on oils in the Siemens tube. He found that an emulsion of oil and gas is formed and made the further striking observation not previously reported that unsaturates behave differently from saturated hydrocarbons in the formation of emulsion and in the effects on the glass wall which he found was rapidly destroyed by unsaturated materials. He found that cyclic and paraffin compounds do not interact to liberate hydrogen and higher paraffin members, but decompose partly into unsaturated compounds.

Vernazza and Stratta (117) found that in silent discharge ethylene alone or mixed with carbon dioxide or air in all cases yielded only saturated hydrocarbons.

Herzog (118) studied the combined action of copper catalysis, heat, pressure and silent electric discharge on acetylene in bringing about its conversion to solid cuprene. He found the presence of oxygen to be advantageous and that a lighter-colored product was obtained from a mixture containing 5–15% of nitrogen.

Linder (I, 21) investigated the behavior of seven normal paraffins in low-voltage glow discharge at pressures of 0.2 to 4.5 mm., 450 volts and 0.5 to 2.5 milliamp., namely: pentane, hexane, heptane, octane, decane, dodecane and *n*-tetradecane. No liquid formed, but a waxlike substance deposited on the cathode. No quantitative analysis was made of the gas, which consisted mostly of hydrogen and lower hydrocarbons. The amount of reaction was proportional to the current, independent of the voltage and vapor pressure. The deposit on the cathode had no influence on the rate of production of gas.

Rowland (119) claimed that the cracking of low-grade oils by silent corona formed a good-quality gasoline with anti-knock properties. Mechanical agitation by the corona was thought to be of first importance.

Stratta and Vernazza (120) specify the following reactions as brought about by silent discharge in ethylene: (1) the condensation of two molecules or more into one; (2) the formation of unsaturated condensation products with or without the liberation of hydrogen; (3) the formation of saturated hydrocarbons by interaction of the hydrogen liberated.

Kleinschmidt (121) described an apparatus for converting benzene to biphenyl and other condensation products, in glow discharge through the substance in a dispersed state.

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CHAPTER VIII

HYDROGEN-CARBON COMPOUNDS CONTAINING OTHER ELEMENTS (1.6.7 TO 1.6.80)

(1.6.7) **Hydrogen cyanide.** In 1869 Berthelot (1) investigated the reaction between acetylene and nitrogen. He found that hydrogen cyanide is formed in the spark, but not (2) in silent discharge. Some decomposition to carbon and hydrogen occurs which can be suppressed by excess of hydrogen. The reaction slows down as an equilibrium is approached between acetylene, hydrogen, nitrogen and hydrogen cyanide. The rate can be sustained if concentrated potash is added to absorb hydrogen cyanide. No ammonia is formed. Hydrogen cyanide is also formed by the sparking of nitrogen and any gaseous hydrocarbon (VII, 52). The reaction between cyanogen and hydrogen with the formation of hydrogen cyanide was also found to take place in the spark. This was later (3) found to be mainly due to thermal action. Montemartini (4) effected the same reaction in the direct current corona.

Brillot (VII, 5) obtained considerable quantities of hydrogen cyanide by the combination of hydrogen and cyanogen in silent discharge, but accompanied by other products to such an extent that he did not regard the conditions favorable for the formation of hydrogen cyanide. He also pointed out the possibility of nitrogen fixation during electrical storms.

Francesconi and Ciurlo (5) studied the reactions of hydrogen cyanide and ammonia with unsaturated organic compounds in silent discharge. With hydrogen cyanide they obtained alkyl cyanides of the type

$$HCN + C_2H_4 \rightarrow C_2H_5CN$$

and with ammonia obtained amines, as

$$NH_3 + C_2H_4 \rightarrow C_2H_5 \cdot NH_2$$

In glow discharge Fischer and Peters (VII, 82) obtained hydrogen cyanide from a gaseous mixture of hydrogen, nitrogen and unsaturated hydrocarbons, as: $C_{10}H_8 + H_2 + 5N_2 \rightarrow 10\ HCN$. Peters and Küster (6) obtained large yields of hydrogen cyanide in low-pressure glow discharge in mixtures of methane and ammonia. In 1:1 mixture, 70% of the maximum yield of hydrogen cyanide was obtained; below 15% of either methane or ammonia, quantitative yield of hydrogen cyanide based on the smaller component was obtained. Excess methane gives acetylene; excess ammonia gives nitrogen and hydrogen. Addition of ammonia to methane in the production of acetylene reduced the amount of free carbon and of tar. From the mixture 3 parts of methane to 7 parts of ammonia pure ammonium cyanide crystallizes out (3 parts hydrogen being formed).

In the treatment of aniline vapor at low pressure in electrodeless discharge Harkins and Gans (VI, 73; see also Chapter VI, page 113) obtained spectroscopic evidence for the existence in the discharge chamber of CN, NH, N_2, and N_2^+.

(1.6.7) **Hydrogen-carbon-nitrogen compounds.** As early as 1860 Buff and Hofmann (VII, 39) decomposed alkyl amines in the electric spark. White crystals of methyl ammonium cyanide ($CH_3 \cdot NH_3 \cdot CN$) first appear. Later blackening indicated decomposition which, however, never became quite complete (5.1 cc. increased to 13.7 cc. whereas complete decomposition to the elements would require 15.3 cc.). Trimethylamine: 3.7 cc. gave 14.4 cc.; theory 18.5 cc. Ethylamine: 5.2 cc. gave 15.1 cc.; theory 20.8 cc.

Berthelot (VII, 51) devoted much attention to the electrical synthesis of nitrogen organic compounds from nitrogen and hydrocarbon gases:

$$100CH_4 + 100N_2 \rightarrow 115H_2 + 3.4CH_4 + 74.1N_2$$

A solid product, $C_8H_{12}N_4$, was formed which turned blue on standing.

With ethane:

$$100C_2H_6 + 100N_2 \text{ (in 24 hours)} \rightarrow$$

$$98.2H_2 + 73.5N_2 + 3.0 \text{ Hydrocarbons}$$

The condensed products $[C_8H_{12}(NH_2)_2]_n$ had a N:C ratio half of that for the methane product.

For ethylene:

$$100C_2H_4 + 100N_2 \text{ (24 hours)} \rightarrow 28.6H_2 + 0.4C_2H_6 + 72.2N_2$$

No acetylene or ammonia was formed. A condensation product similar to the others in appearance was formed which had an alkaline reaction and an odor of roasted cocoa. The product $C_{16}H_{32}N_4$ has an empirical formula very close to that of the ethane product. The volume of nitrogen fixed is very near to that of hydrogen liberated.

The first behavior of acetylene in the presence of nitrogen is to polymerize as if alone. This is quite parallel to their behavior under alpha radiation (I, 7), where it was found, however, that the rate is enhanced in proportion to the additional ionization of nitrogen. Berthelot showed that in electrical discharge nitrogen later adds to the polymer to the extent of 11.4 volumes of the original 100 volumes of hydrogen (and 100 volumes of original acetylene). The product $C_{18}H_{18}N_2$ is the same as for benzene and quite different from the nitrogen-containing products of other hydrocarbons.

In the case of propene and nitrogen Berthelot (VII, 51) again found rapid condensation followed by slow absorption of nitrogen:

$$100C_3H_6 + 100N_2 \rightarrow 17.2H_2 + 60.5N_2.$$

The product has the formula $C_{15}H_{28}N_4$ or $C_{15}H_{20}(NH_2)_4$. The volume of nitrogen absorbed is twice that of the hydrogen liberated.

Trimethylene behaved similarly:

$$100C_3H_6 + 100N_2 \rightarrow 41.4H_2 + 1.6CH_4 + 61.4N_2.$$

The product is $C_{15}H_{18}(NH_2)_2$.

Allylene and nitrogen gave a condensation product $C_{15}H_{20}N_2$, no free hydrogen, no hydrocarbons, no ammonia.

In a reexamination of methylamine in the spark, Berthelot (VII,52) found hydrogen cyanide, acetylene, hydrogen and carbon as products.

Losanitsch (7) subjected ammonia and isobutane to ozonizer discharge and obtained an insoluble oil (C_nH_{2n}) and amines soluble in hydrochloric acid. The free base appeared to be hexylamine ($C_6H_7 \cdot NH_2$). With *n*-hexane a similar base was obtained, but most of the reaction is to form a mixture of paraffin and olefin hydrocarbons boiling between 40 and 100° at 13 mm. pressure.

Briner and Durand (8) sparked a mixture of nitrogen and ethane at 15°, −78° and −192° C. The products were carbon, hydrogen, ammonia, hydrogen cyanide and higher hydrocarbons which absorb ammonia or hydrogen cyanide to form addition compounds. At −78° C. a mixture of $2\ N_2 + 1\ C_2H_2$ gave hydrogen cyanide, more ammonia, a little hydrogen and a liquid containing nitrogen. Unsaturated hydrocarbons were found to give more hydrogen cyanide than the saturates do. Ethane as well as a mixture of ethane and nitrogen gave higher hydrocarbons.

Miyamoto (9) found that a mixture of ethylene and nitrogen in effluve gave a nitride, $C_{18}H_{31}CN_2$, and a product $C_{20}H_{38}N_4O_2$, probably from $C_{20}H_{38}N_4$ and unsaturates, $C_{10}H_{20}$, $C_{12}H_{22}$, $C_{13}H_{24}$, $C_{15}H_{28}$,

$C_{18}H_{34}$. The gaseous products included acetylene and hydrogen cyanide. After several months the inside of the vessel is covered with an oxidized polymer $(C_{22}H_{34}O_2)_n$. A mixture of benzene and carbon dioxide formed a phenolic compound $C_{30}H_{30}O_9$.

Fowler and Mardles (VII, 69) attacked liquid aniline by means of a submerged spark obtaining monomethyl and dimethylaniline.

(1.6.7.8) **Hydrogen-carbon-nitrogen-oxygen comopunds.** Berthelot (VII, 51) examined the behavior and products in silent discharge from mixtures of nitrogen with alcohols, ethers and phenols. Hydrogen evolution parallels that from corresponding hydrocarbons in point of chemical saturation. Nitrogen molecules seem to substitute one hydrogen atom in many cases. Those compounds which lose little hydrogen take on but little nitrogen.

Berthelot (1–3) further found in general that aldehydes fix hydrogen more readily than the corresponding alcohols. The evolution of hydrogen is less marked in aldehydes than in alcohols and hydrocarbons. The amount of nitrogen fixed diminishes with the degree of condensation of polymeric compounds.

Generally the organic acids fix nitrogen in the effluve, but without loss of hydrogen, or practically none, as manifested in a less degree by the aldehydes. Acetic and propionic acids fix about 1.5 atoms of nitrogen each per molecule. One atom of nitrogen goes into the acid, and the rest combines with water liberated to form ammonium nitrite. The limiting reaction for acids $C_nH_{2n}O_2$ would be $C_nH_{2n-4} + H_2O$. Quantities of carbon monoxide or dioxide produced are negligible. The esters fix more nitrogen than the acids and also liberate carbon monoxide and dioxide. Great differences were observed between maleic and fumaric acids in behavior. Maleic fixed no nitrogen but fumaric did. Fumaric liberated no carbon monoxide nor dioxide but maleic liberated both, about seven times as much monoxide as dioxide.

According to Berthelot (11), most organic compounds containing nitrogen will in silent discharge (effluve) fix more nitrogen. Exceptions are ethyl and allyl amines) phenylhydrazine and ethyl and propyl diamines. Losanitsch (40) obtained a thick, dark red, clear liquid with unpleasant aminelike odor from a mixture of ether and ammonia in silent discharge. The basic material, $C_9H_{17}N_3O$, was soluble in water and gives a salt with hydrochloric acid.

Löb (12), subjecting the vapors of formamide to effluve, obtained the reaction: $2HCO \cdot NH_2 \rightarrow H_2 + (CO \cdot NH_2)_2$ with the evolution of some carbon monoxide and ammonia. At 40° with a 5% solution of formamide, the compounds $H_2NOC \cdot CO_2NH_4$ and $(CO_2 \cdot NH_4)_2$ were obtained, also a test for a small amount of aminoacetic acid. Tests for amino acids were also obtained from moist carbon monoxide and ammonia, which was the first time this synthesis was ever accomplished.

Pieters (13), passing coke-oven gas through a number of water-cooled ozonizers at a rate of 150 liters per hour, formed a condensate soluble in alkali, insoluble in benzene, containing 44% carbon, 7.4% hydrogen, 0.6% nitrogen, having an odor of formaldehyde and tending to form a resin. Some nitrogen dioxide was also formed in the ozonizer.

Crippa and Gallotti (VI, 54) activated a mixture of hydrogen and nitrogen by passage through silent discharge, then mixed it with carbon monoxide and passed it at atmospheric pressure through tubes at 115–120° C. Urea is deposited from the issuing gases. The authors affirm it is not a case of carbon monoxide diffusing back into the discharge zone and being subjected there together with hydrogen and nitrogen to direct electrical action.

(1.6.7.16) **Hydrogen sulphocyanide.** Gluud and Dieckmann (10) examined the reaction in *aqueous* solution

$$\mathrm{HCNS} \rightarrow \mathrm{HCN} + \mathrm{S}\ \text{(rhombic)}$$

in both silent and glow discharge. In the former the yield was low and the energy consumption very high. In glow discharge with hydrogen added the chemical yield was 80% but the efficiency was low, 675 watt-hours per gram mole of hydrogen cyanide, compared with theoretical 6.87 watt-hours. Some hydrogen sulphide, sulphur dioxide and free sulphur were also produced.

(1.6.8) **Compounds of hydrogen, carbon and oxygen.** In mixtures of gases containing these three elements, such as carbon monoxide and carbon dioxide and water or hydrogen or methane, one obtains in electrical discharge a variety of reactions of decomposition and synthesis, of oxidation and reduction. The general trend is toward condensation to higher polymers of very complicated character. There are two general reasons for this type of predominant reaction. The higher products with low vapor pressure condense as liquid or solid products, hence pass out of the field of action and undergo no further or at most only slight reaction. The activation in electrical discharge is effected by electronic bombardment of individual molecules in which high amounts of activation energy are delivered in a single collision without the necessity of high temperature or a general intermolecular interchange of energy. Such condition is conducive to the formation of large molecules without their being subsequently shattered at high temperature or by repeated collisions. In other words, these relatively cold reactions have the activating influence of high temperature without its dissociating effect.

As early as 1869 Berthelot (VII, 37) studied what he called the equilibrium between hydrogen, water, carbon monoxide, carbon dioxide and oxygen in spark discharge. He claimed that mixtures which are not at first explosive for a single spark become so on prolonged action. In silent discharge Maquenne (14) claimed to bring about the reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

in which formic acid might be an intermediate addition product. He also found (15) that methanol was decomposed to yield carbon monoxide, carbon dioxide, methane, acetylene, ethylene and hydrogen; that ethyl alcohol gave the same and ethane in addition; that acetone gave carbon monoxide, ethane, hydrogen, ethylene, carbon dioxide; and acetic acid gave carbon monoxide, hydrogen, methane, carbon dioxide and ethylene.

Löb (16) made an extended study of reactions of this class both in alternating- and direct-current silent discharge. In direct current he found that water and carbon dioxide reacted to yield carbon monoxide, formic acid and oxygen, together with hydrogen peroxide and ozone. (The latter two were absent when alternating current was used.) In both alternating and direct current he found that carbon monoxide and water reacted to form carbon dioxide and hydrogen, which reaction was not repressed by excess of carbon dioxide or of hydrogen, and therefore did not have the character of thermal equilibrium subject to mass action. He found that the formation of formaldehyde from hydrogen and carbon monoxide took place more slowly than the reaction

$$H_2 + O_3 \rightarrow H_2O_2 + O$$

In a mixture of carbon dioxide and water he found the following five simultaneous reactions:

$$2CO_2 \rightarrow 2CO + O_2;\ CO + H_2O \rightarrow H{\cdot}COOH;\ CO + H_2O \rightarrow CO_2 + H_2;\ H_2 + CO \rightarrow H{\cdot}CHO;\ 3O_2 \rightarrow 2O_3;\ 2H_2 + 2O_3 \rightarrow 2H_2O_2 + O_2$$

$$2CO + H_2O + H_2 \rightarrow H{\cdot}CHO + H{\cdot}COOH + (CH_2OH{\cdot}CHO).$$

The glycol aldehyde ($CH_2OH{\cdot}CHO$) easily polymerizes to sugars. Also $CH_4 + H_2O \rightarrow CO + 3H_2$; $CO + H_2 \rightarrow H{\cdot}CHO$; $CO + CH_4 \rightarrow$

$CH_3 \cdot CHO$; $CH_3 \cdot CHO + H_2 \rightarrow C_2H_5OH$. $CH_4 + CO_2 \rightarrow CH_3 \cdot COOH$ was absent.

$$H \cdot CHO \rightarrow CO + H_2;\ HCOOH \rightarrow CO + CO_2 + H_2.$$

In the electrical decomposition of ethyl alcohol Löb (16) found 68 parts by volume of hydrogen, 22 of methane and ethane, 8 of ethylene, 5 of carbon monoxide and 1 of carbon dioxide.

$$CH_3 \cdot CHO \rightarrow CO + CH_4 \rightarrow H_2 + \text{etc.}$$

$$CH_3 \cdot COOH \rightarrow CO_2 + CO + H_2 + CH_4 + C_nH_{2n}$$

Losanitsch and Jovitschitsch (VII, 54) used the ozonizer to investigate a large number of reactions involving compounds of hydrogen, carbon, and oxygen. They formulate the following:

$$CO + H_2O \rightarrow H \cdot COOH$$

$$CO_2 + H_2O \rightarrow H \cdot COOH + H_2O_2 + O$$

$$CO + H_2 \rightarrow H \cdot CHO \rightarrow CH_2OH \cdot CHO \rightarrow (CH_2OH \cdot CHO)_n$$

The last reaction should be compared with the results of Brodie (IV, 31) in spark discharge where he found complete reduction of CO to CH_4:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

Further reaction claimed by Losanitsch (17):

$$CO_2 + H_2 \rightarrow HCOOH;\ CO + CH_4 \rightarrow CH_3 \cdot CHO$$

$$CO + \text{higher hydrocarbons} \rightarrow \text{higher alcohols}$$

Collie (18) used silent discharge in the ozonizer to attempt the addition of CO and C_2H_4. Liquid was readily obtained which on fractionation gave indications of aldehyde and acrolein. The main part of the reaction, however, consisted in the polymerization of C_2H_4 to a liquid olefin about $C_{10}H_{20}$. The liberation of hydrogen also gave evidence of the production of some still less saturated hydrocarbons.

Losanitsch (VII, 62) used silent discharge in the ozonizer to study the reactions of a variety of organic vapors and gases. Ether underwent a rapid reaction to gaseous and liquid products. The gases consisted of 80% methane and 20% hydrogen and a little carbon monoxide and unsaturates. The mobile yellow liquid gave a strong reaction of aldehydes. The general course of the gas reaction is:

$$(C_2H_5)_2O \rightarrow H \cdot CHO + CH_4 + C_2H_4$$

$$H \cdot CHO + (C_2H_5)_2O \rightarrow CH_2(OC_2H_5)_2;\ \text{(ethylal)}$$

The direct condensation of ether yields C_4H_8O by doubling and elimination of water, and $C_8H_{14}O_2$ by elimination of both water and hydrogen.

Acetaldehyde gave a gas (80%) and a liquid (20%).

$$CH_3{\cdot}CHO \rightarrow CH_4 + CO + H{\cdot}CHO.$$

Formaldehyde polymerized further.

Formic acid decomposed to carbon monoxide and water. Acetic acid gave carbon monoxide, water and a tar.

Ethyl acetate gave carbon monoxide, methane, hydrogen and a yellow liquid containing aldehyde.

Besson and Fournier (19) treated acetaldehyde in a current of hydrogen in silent discharge and fractionated the liquid products by distillation. The following reactions were indicated:

$$2CH_3{\cdot}CHO \rightarrow C_2H_4 + CH_3{\cdot}COOH$$

$$4CH_3{\cdot}CHO \rightarrow 2C_2H_4 + C_2H_5{\cdot}COOH + H{\cdot}COOH$$

$$2CH_3{\cdot}CHO \rightarrow H_2 + CO + CH_3{\cdot}CO{\cdot}CH_3$$

$$3CH_3{\cdot}CHO \rightarrow 2H_2 + 2CO + C_2H_5{\cdot}CO{\cdot}CH_3$$

$$2CH_3{\cdot}CHO \rightarrow H_2 + CH_3{\cdot}CO{\cdot}CO{\cdot}CH_3$$

Losanitsch (VII, 62) studied the addition of carbon monoxide and hydrogen in silent discharge. He obtained a yellow product of which a small part is an oily liquid soluble in alcohol. The major portion, soluble in water, analyzes for $C_{12}H_{18}O_{11}$, the anhydride of $(C_6H_{10}O_6)_2$. On dissolving in water it hydrolyzes to $CHO{\cdot}CHO{\cdot}(CH_2OH{\cdot}CHO)_2$, the molecular weight of which was determined by the freezing-point method.

Lōb and Sato (20) found that the hydrolysis of starch is promoted by silent and by glow discharge both with and without the presence of oxygen. Part of the starch is changed (polymerized) so that its attack by diastase is hindered. Casein and fibrin were found not to be affected. The tryptic properties of pancreatin were diminished. The lipase of pancreatin is weakened.

The hydrolysis of cane sugar was found by Lōb (21) to be promoted by silent discharge. Two 50-cc. portions of 2.5% sugar solution originally containing 48.2 and 57.2 mg. of reducing sugar after 12 hours' treatment contained 110 and 302.4 mg., respectively. In 30 hours acid formed to the extent of 0.35 cc. of 0.1 *N* sodium hydroxide solution. Secondary decomposition by hydrogen peroxide was prevented by working in a vacuum of 20 mm.

Eichwald (22) treated pure oleic acid in glow discharge. The iodine number falls, the molecular weight rises and stearic acid is produced corresponding to the drop in iodine number. Hydrogen is split out, giving highly unsaturated acids which polymerize. Hydrogen combines with oleic to give stearic acid.

In direct-current semi-corona consisting of a metal thread 1 meter long suspended in the axis of a glass tube, Montemartini (4) obtained the following incomplete reactions:

$$CO + H_2O \rightarrow CO_2 + H_2; \quad CO_2 + H_2 \rightarrow H \cdot CHO + H_2O;$$

$$C_6H_6 + CO_2 \rightarrow C_6H_5 \cdot COOH$$

In 1923, from analogy with similar reactions of Lind and Bardwell (23) under alpha rays, Lind (24) attributed such reactions in electrical discharge as $CO_2 + H_2 \rightarrow H \cdot CHO + H_2O$ to the "acceptance" of the ion CO_2^+ by hydrogen (or of carbon dioxide by H_2^+) rather than to reduction of carbon dioxide merely by some activated form of hydrogen.

Lunt (II, 15) used high frequency (1.5×10^7 cycles) to study the equilibrium

$$H_2 + CO_2 \rightleftharpoons H_2O + CO$$

which he found at 77.5% of the reaction from left to right and to be independent of voltage and the power input. For hydrogen to carbon dioxide ratios greater than 2, some methane is also formed but not equivalent to the carbon monoxide that should have been formed. For hydrogen to carbon dioxide ratios less than 1.25, some oxygen is liberated. The "temperature equivalent" of the equilibrium is 800 to 1200°. No formaldehyde or formic acid could be detected (VII, 54; II, 16) (see also Chapter II, page 53).

Using glow discharge in a Siemens tube, Koenig and Weinig (25) found that water gas reacts to form water, carbon dioxide, formic acid, formaldehyde and $CH_2OH \cdot CHO$. To obtain the maximum yield (77%) of formaldehyde the walls of the tube were periodically washed with water to prevent accumulation of reaction products and consequent reversal of the reaction. The maximum yield for 46% carbon monoxide in the entering gas was 2 grams of formaldehyde per kw-hr.

In electrodeless discharge Moens and Juliard (VII, 70) found that a mixture of carbon monoxide and hydrogen expands 6% but returns to the original volume after cessation of discharge, even in the presence of concentrated sulphuric acid. Alcohols and ethers were decomposed in electrodeless discharge to threefold of the volume of original gases.

Hiedemann (26) examined the behavior of a number of organic compounds in high-frequency glow discharge and gave a detailed description of the electrical phenomena. For all substances he found decomposition and deposition of a highly polymerized inert solid from vapors of ether, ethyl alcohol, acetone, chloroform, carbon tetrachloride and ethane. The gaseous products were not analyzed.

Using metal electrodes at 5000–6000 volts Peters and Pranschke (27) subjected mixtures of methane and water vapor, and methane and carbon dioxide to the discharge with a flow of 800 liters per hour. Decomposition to carbon monoxide and oxygen was complete. No free carbon was separated. At lower voltage most of the methane was converted to acetylene. By varying the mixtures a wider variation of the products is obtained.

Rice and Whaley (28) found that the following organic compounds by passage through electrodeless discharge are cracked to fragments which removed antimony and lead mirrors: n–C_4H_{10}, n–C_5H_{12}, C_2H_4, CH_3OH, C_2H_5OH, CH_3CHO, CH_3COOH and $(CH_3)_2CO$. Mirrors of zinc and cadmium were not removed, which might indicate that hydrogen atoms were the active agent. However, CH_3-groups were identified in the products by the X-ray powder method.

Fischer and Peters (29) give a method of converting water gas quantitatively into condensible hydrocarbons consisting of circulating the gases carbon monoxide and hydrogen through the discharge and then through a freezing tube held at various temperatures. At liquid-air temperature acetylene and ethane predominate; at higher temperatures, higher hydrocarbons in addition to water and carbon dioxide. In a mixture $CO + H_2 + N_2$, conversion to ammonia and hydrogen cyanide attains 80–90%.

According to Jaeger (30), electronic discharge may be used to produce mono- from polycarboxylic compounds in the vapor phase at elevated temperatures.

The reactions of ethyl alcohol were investigated quite early. In 1853 Masson (31) stated that its reaction is partly polar (electrical) and partly thermal. In 1858 Quet (32) found that alcohol under sparking becomes acid and decomposes faster if alkali is added. Resinous material and gas, including carbon monoxide, are produced. He (32) further found a detonating solid to be produced if the gases are passed into ammoniacal copper or silver solution (presumably acetylides of copper and silver).

Perrot (33) obtained free carbon and a resinous material, but no methane by sparking ethyl alcohol. Later he (34) decomposed ethyl alcohol, ether and acetic acid each at the rate of 3 liters of gas evolved per hour.

In 1897 de Hemptinne (35) exposed a variety of organic liquids to alternating electrical discharge ("Schwingungen") and determined carbon dioxide, carbon monoxide and hydrogen in the gases evolved. The substances were methyl, ethyl, *n*-propyl, isopropyl and allyl alcohols, acetaldehyde, acetone, acetic acid, formic acid, propionic aldehyde, *p*-acetaldehyde, methyl acetate, glycerin, glyceric acid, ethylene glycol, glyoxal, lactic acid, oxalic acid, benzene, phenol and benzoic acid.

Berthelot (36), sparking 10 cc. of absolute alcohol for 24 hours, obtained 30.1 cc. of hydrogen, 3.9 cc. of ethane and some aldehyde produced in the liquid. Formaldehyde gave as transitory action methane, hydrogen, carbon monoxide and carbon dioxide, but finally no gases remained except hydrogen and nitrogen. Berthelot (VII, 52) later stated that ternary compounds containing carbon, hydrogen and oxygen are ultimately destroyed in the spark but with the immediate and transitory formation of acetylene. The oxygen is distributed between water, carbon monoxide and carbon dioxide.

From methyl alcohol P. and A. Thenard (37) obtained methane, hydrogen, acid and a resin on sparking. Maquenne (14) obtained carbon monoxide, carbon dioxide and hydrogen from formic acid; water and carbon monoxide react to reach an equilibrium

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

with about 3% of carbon monoxide.

In silent discharge Löb (38) obtained some butyric acid from ethyl alcohol by a predicated sequence of reactions:

$$2C_2H_5OH \rightarrow H_2 + 2CH_3\cdot CHO$$

$$2CH_3\cdot CHO \rightarrow CH_3\cdot CHOH\cdot CH_2CHO \rightarrow CH_3\cdot CH_2\cdot CH_2\cdot COOH$$

Comanducci (39) oxidized methyl and ethyl alcohols by means of oxygen in the effluve to formic and acetic acids, respectively. Either acetaldehyde or paraldehyde is oxidized by oxygen to acetic acid. But ether and acetone he found not to be oxidized by oxygen, while acetaldehyde is reduced by hydrogen to ethyl alcohol.

Losanitsch (40) treated methylal in silent discharge and obtained a variety of products: $CH_2(OCH_3)_2 \rightarrow CO$, CH_4, H_2, unsaturated hydrocarbons and liquids with the following empirical formulas and boiling points: $C_3H_8O_3$ (95°–105°); $C_7H_{18}O_6$ (110°–120°);

(110° – 120° at 16 mm.); $(C_3H_6O_2)_n$ (140° – 150° at 16 mm.). He found that acetal gave the same gaseous products and the following liquids: $C_6H_{12}O_2$ (100° – 110°); $C_{16}H_{30}O_5$ (140° – 200°); $C_{14}H_{22}O_4$ boiling above 200° and all at 16 mm. pressure. All the liquids had odor and properties of alcohols.

Löb (41) exposed aqueous starch solutions in glass and porcelain vessels to silent discharge. He observed conversion to sugar and the acquisition of strong reducing properties.

Poma, Bassi and Nesti (42) have investigated the reactions produced in vapors of alcohols, ketones and acids by both the spark and silent discharge. Gas analyses showed the abundance of hydrogen, carbon monoxide, carbon dioxide, acetylene, methane, ethane, etc., among the gaseous products. Poma and Bassi (42) established that the proportion of methane increases with the prevalence of methyl groups in the initial compounds, just as Schoepfle, Connell and Fellows (IV, 48, 49) found to be the case under cathode-ray bombardment of hydrocarbon liquids.

Fowler and Mardles (VII, 69) observed the decomposition of ethyl alcohol vapors in the spark.

De Hemptinne (43) reduced oleic to stearic acid by hydrogen at reduced pressure in silent discharge.

A French patent (694,330, April 23, 1930) assigned to Gutehoffnungshüte Oberhausen A.G. claimed that the addition of carbon monoxide and methane in high-tension high-frequency discharge produced formaldehyde.

Losanitsch (44) transformed aniline into a yellowish brown liquid (with evolution of carbon monoxide and hydrogen) which on distillation yielded two substances with empirical formulas $(C_5H_{10}O_2)_2$ and $(C_6H_{10}O_2)_4$, both of which had properties of aldehydes.

Davis (VII, 98) found in the decomposition of acetone in brush discharge that the whole molecule is converted to gases, the principal reaction being: $(CH_3)_2CO \rightarrow C_2H_6 + CO$. The hydrogen, acetylene and ethylene which were found come from the decomposition of ethane. Ketene $(CH_2 \cdot CO)$ is also produced as in pyrolysis.

Lefebvre and Overbeke (45) studied the reactions of a mixture of carbon monoxide and hydrogen in the condensed spark. The products were water vapor, carbon dioxide and acetylene. Between 20% and 80% of either reactant, at a total pressure less than 9 mm., there was not much reaction unless the products were removed as soon as formed.

Finch, Bradford and Greenshields (46) studied the equilibrium:

$$CO + O_2 + H_2 \rightleftharpoons CO_2 + H_2O$$

as established in the direct-current cathode zone between platinum or gold electrodes. The pressure dependence indicated the superposition of two equilibria differently affected by pressure:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \text{and} \quad 2CO + 2OH \rightleftharpoons 2CO_2 + H_2$$

Iwamoto (47) observed that fatty acids in low-pressure hydrogen in silent discharge undergo polymerization, dehydration and dehydrogenation. Helium produces the same result; also nitrogen, but more slowly; carbon monoxide, sulfur dioxide, acetylene and hydrogen sulphide have an inhibitory reaction.

Brewer and Kueck (I, 17) studied the oxidation of methane by oxygen in glow discharge. In a mixture of 1 CH_4 to 2 O_2 reaction is complete to water and carbon dioxide. No hydrogen peroxide is formed, which is to be contrasted with the interaction of hydrogen and oxygen in glow discharge (I, 15). The rate of oxidation is greater with excess of methane, less with excess of oxygen and still less in the presence of argon. It is concluded that the methane ion (CH_4^+) alone is effective and the total yield of water plus carbon dioxide molecules is 6 or 7 per methane ion.

Further work on hydrogen-carbon-oxygen compounds is reported by Linder and Davis (VII, 122). Methyl, ethyl, butyl and hexyl-alcohol, glycerol and sucrose show an increase of rate of gas and solid production with increase in molecular size. The rates are comparable with the similar decomposition rates of the paraffins. The types of gases given off by the paraffins are also given off by the oxygen-containing compounds with the addition of carbon monoxide and dioxide. Aldehydes, water and acids are found in the liquid products in increasing amount, depending on the proportion of oxygen in the original compound. The electrical conductivity of the alcohols increases on passage through the discharge. Cellulose in the form of cotton wrapped around the cathode shows deterioration under electrical discharge in hydrocarbon vapors. Water is produced. The decomposition may be mostly of thermal origin. The results of these studies are summarized in Table 18.

(1.6.16) **Hydrogen-carbon-sulphur compounds.** Berthelot (VII, 6) introduced the vapors of sulphur-organic compounds including alcohols and ethers into the electric spark and obtained decomposition to carbon, sulphur, hydrogen sulphide, acetylene and hydrogen.

Losanitsch (VII, 62) found that the treatment of dimethyl sulphide in the ozonizer gave a gas phase and an insoluble liquid containing

S_4, $C_7H_{14}S_6$ and $C_7H_{16}S_5$.

TABLE 18

Decomposition of Oxygen-Containing Compounds in Glow Discharge

E. G. Linder and A. P. Davis (VII, 122)

	Alcohol				Glycerol	Sucrose	Cellulose with	
	Methyl	Ethyl	Butyl	Hexyl			Toluene	Decane
Gas production:								
dp/dt (mm./sec./ma.) × 10^6	439	570	546	644	640	668		
Solid production:								
gm./sec./ma. × 10^6	0.114	0.120	0.280	0.560	0.310	0.290		
Gas production:								
Per cent hydrogen	58.3	49.6	44.9	43.8	43.2	32.4	41.0	48.9
Per cent acetylenes	2.0	8.7	6.7	7.9	3.5	2.9	13.1	4.6
Per cent ethylenes	8.3	18.8	34.5	27.2	8.6	3.9	18.4	12.8
Per cent paraffins	10.6	9.3	10.5	10.1	2.7	4.2	5.3	12.9
Per cent carbon dioxide	1.1	1.6	1.2	3.8	2.3	9.7	6.3	2.9
Per cent carbon monoxide	19.8	12.0	2.2	7.2	39.7	46.9	15.3	17.9
Aldehyde	Negative	Faint	Negative	Negative	Strong	Faint		
Formaldehyde	Positive	Positive	Negative	Negative	Weak	Negative		
Acidity	Neutral	Neutral	Neutral	Neutral	Acid (weak)	Acid (strong)		
Water	Negative	Negative	Negative	Negative	....	Negative	0.06	0.10
Copper number:								
Before	......	......	......	......	....	....	0.029	0.3
After	......	......	......	......	....	....	0.029	0.7
Specific conductivity × 10^6 ohms^{-1}:								
Before	1.52	0.65	0.28	0.12	10^{-4}			
After	15.20	1.44	0.60	0.125	10^{-4}			

(1.6.17) **Hydrogen-carbon-chlorine compounds.** Besides the investigations which are not very numerous of chlorine-containing organic compounds under the influence of electrical discharge, their behavior in the magnetic field is also included.

Berthelot (VII, 48) treated methyl chloride in silent discharge (effluve) and observed the production of hydrogen chloride, some acetylene and a hydrocarbon like ethane. He assumed the reactions to be:

$$2CH_3Cl \rightarrow C_2H_6 + Cl_2 \quad \text{and} \quad 2Cl_2 + C_2H_6 \rightarrow C_2H_2 + 4HCl$$

Later hydrogen chloride and acetylene disappear, leaving hydrogen and chlorinated hydrocarbons which get their chlorine in part from hydrogen chloride.

Chloroform gave hydrogen chloride and a heavy liquid which on distillation yielded an oily fraction and later white crystals of hexachloroethane (C_2Cl_6). Hydrogen and carbon tetrachloride give the same reactions as chloroform.

Besson and Fournier (48), also using an ozonizer, found that chloroform gave a liquid which on fractionation yielded tetrachloroethylene (C_2Cl_4), pentachloroethane (C_2HCl_5), hexachloroethane (C_2Cl_6) which predominated, hexachloropropylene (C_3Cl_6), heptachloropropane (C_3Cl_7H), and octochlorobutylene (C_4Cl_8). Methyl chloride (without hydrogen) in a series of discharge tubes in a battery gave hydrogen, dichloroethane ($C_2Cl_2H_4$), trichloropropane ($C_3Cl_3H_5$), and trichlorobutylene ($C_4Cl_3H_5$); in general, two series of saturates and unsaturates.

Regnault (49) examined the effect of sparking dichlororethane ($C_2H_4Cl_2$) and found the production of "liqueur des Hollandais" accompanied by no change in pressure.

Losanitsch (44) investigated the products formed by the addition of hydrogen chloride to unsaturated hydrocarbons in electrical discharge.

The production of solid condensates from chloroform and tetrachloride by high-frequency glow discharge was observed by Hiedemann (26). The gaseous products were not examined. With ethylene, acetylene and benzene the glow discharge formed highly condensed products with some cleavage of hydrogen. Equal volumes of hydrogen chloride and ethylene yielded dichloropentane ($C_5H_{10}Cl_2$). One volume of acetylene with two volumes of hydrogen chloride condensed rapidly to trichlorobutane ($C_4H_7Cl_3$) and tetrachlorobutane ($C_4H_6Cl_4$). Benzene and hydrogen chloride gave dichlorodihydrochlorobenzene ($C_6H_7Cl_3$).

Clark and his collaborators (50, 51) carried out the following organic reactions under influence of the magnetic field using a Weiss electromagnet of 23,000 gauss. The addition of hydrogen bromide to allyl bromide in glacial acetic acid solution gives only 20% of the trimethylene compound as compared with more than 50% without the field, the rest of the addition in each case being propylene bromide. On the other hand, neither magnetic nor electric fields influenced the addition of hydrogen bromide to 2-pentene in the vapor phase. The difference consisted in the absence of a polar solvent and of a polar reactant such as allyl bromide. Also the action of nitric acid on benzoic acid was not changed appreciably by the magnetic nor the electric field.

Methyl chloride, ethyl chloride and other alkyl chlorides are decomposed in the electric spark to hydrogen halide, acetylene, hydrogen and carbon (Berthelot, VII, 52).

(**1.6.35**) **Alkyl Bromides.** These substances decompose under sparking to give bromine, hydrogen bromide, acetylene and carbon (Berthelot, VII, 52).

(**1.6.53**) **Alkyl Iodides.** These compounds decompose in the electric spark to iodine, carbon and acetylene (Berthelot, VII, 52).

(**1.6.80**) **Hydrogen-Carbon-Mercury Compounds.** In 1900 Berthelot (52), in studying the ability of the inert gases to enter into chemical combination, introduced a mixture of mercury dimethyl and argon into silent discharge. No argon was condensed, but the mercury dimethyl was decomposed to methane, a little ethane, hydrogen and mercury. In a mixture of mercury dimethyl and nitrogen 22% of the nitrogen was fixed in a compound of approximate empirical formula C_4H_7N. In a mixture of argon and mercury diphenyl, 3.8% of the argon was fixed in 20 hours.

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CHAPTER IX

HYDROGEN COMPOUNDS CONTAINING ELEMENTS OTHER THAN CARBON. (1.7 TO 5.17)

(1.7) **Ammonia synthesis and decomposition.** The behavior of ammonia in electrical discharge differs markedly from that of methane and the other hydrocarbons in showing so little tendency toward condensation or the formation of chain compounds, hydrazine in small amounts being the only exception.

The earliest observation of the decomposition of ammonia by the spark is attributed to Marum by Morveau and Seguin in an article on "Air" in the "Nouveau dictionnaire encyclopédique" and also referred to in 1790 in the "Annales de chimie" (Vol. 7, p. 73). Davy (1) in 1808 proved the composition of ammonia by decomposing it in the spark. Its decomposition was also noted by Sainte-Claire-Deville (2) and by Buff and Hofmann (VII, 39) in the spark, by Perrot (3) in the condensed spark and by de Hemptinne (VII, 50) in oscillatory discharge.

There is some doubt as to the earliest synthesis of ammonia in the spark. Without citing his authority Regnault mentioned it in his "Traité eléméntaire de chimie" (Vol. I, p. 172), which was confirmed by Morren (4) in 1859, also in the spark, and by P. and A. Thenard (VII, 3) in silent discharge, who found the synthesis to be much more rapid in the presence of sulphuric acid. This can be readily understood in the withdrawal of the synthesized ammonia from the decomposing action of the discharge. Chabrier is also cited as one of the early investigators of ammonia synthesis in effluve. Donkin (5) observed the synthesis of ammonia in the effluve by absorption in hydrochloric acid and a Nessler test.

In 1877 Berthelot (VII, 6) allowed the discharge from a high-potential Ruhmkorff coil to pass through nitrogen gas over water and observed the formation of ammonium nitrite. In 1880 Berthelot (6) reviewed the early history of the electrical synthesis of ammonia, which he again referred to in 1901 (VII, 52). De Hemptinne (VII, 50) studied also the synthesis of ammonia in oscillatory discharge.

Both decomposition and synthesis of ammonia were observed in the effluve by P. and A. Thenard (VIII, 37), who suggested the existence of an equilibrium or steady state, which had been previously inferred by Sainte-Claire-Deville, who found that the decomposition of ammonia even in the spark is not quite complete since a fog could be detected with hydrogen chloride. This was reached in the effluve from both directions by Berthelot (7; VII, 48) in 1876 and determined to be at 3% of ammonia synthesis. On the contrary, Berthelot (7) found the decomposition of ammonia in the spark to go completely to the elements.

In his study of this reaction in oscillatory discharge de Hemptinne found that reduced pressure of gas produced greater dissociation of ammonia but not in rigid accord with the law of mass action. Also excess of either hydrogen or nitrogen depressed dissociation but again not in quantitative agreement with mass action.

Briner and Mettler (8) studied the variables which affect the synthesis of ammonia in the spark. They avoided decomposition by freezing out the ammonia with liquid air. The maximum rate occurs at 100-mm. pressure, owing to two opposite effects—increase of electrical conduction with diminishing pressure, and the mass-action effect favorable to synthesis at higher pressures. The equilibrium was found to be at 3–4% of ammonia. At the optimum pressure the yield was 0.17 gram of ammonia per kilowatt-hour in the primary circuit. A Wehnelt interruptor and platinum electrodes close to one another were found to give the best spark. The ammonia production was evenly distributed in the spark. The most active mixture was $3H_2:N_2$. Excess of hydrogen was less inhibitive than excess of nitrogen. (This is perhaps to be interpreted in terms of their relative "stopping powers.")

Synthesis in the arc (with liquid air) was found to be very active, and again the optimum pressure was 100 mm. The effluve in liquid air was found to be better than the spark for synthesis of ammonia, the opposite being true at ordinary temperature. In the presence of sulphuric acid at ordinary temperature the effluve is just as effective as with liquid air, thus showing that the quick removal of ammonia from the field of action is the controlling factor. The theory is proposed by Briner and Mettler (8) that both hydrogen and nitrogen are dissociated to their atoms, which then combine in part to form ammonia.

In 1902 de Hemptinne (9) found that higher pressure is favorable to ammonia synthesis in the spark; higher temperature is unfavorable. But in silent discharge both higher pressure and higher temperature are unfavorable. Smits and Aten (10) also observed the synthesis and decomposition of ammonia in silent discharge.

In 1906 Pohl (11) used a Siemens tube to study the decomposition of ammonia. He found that Faraday's law is not applicable. The quantity of current (in the secondary) necessary to decompose one mole of ammonia is much less than 96,500 coulombs. Depending upon conditions it was found to be only 1950 to 6500 coulombs. The yield of decomposition increases with pressure but decreases with water content of the gas, and with current density and potential which had an optimum at about 7000 volts. The decomposition was 1.3 to 2.5 grams per hp-hr., greatest for low voltage, high pressure and large surface. The reaction was first order with respect to pressure. The equilibrium, approached by synthesis, was found to lie at 2.4 to 2.8% of ammonia.

Le Blanc (12) reported experiments of Davies, using methods similar to those of Pohl, which showed that the decomposition of ammonia in silent discharge follows the first order initially but as the reaction proceeds with the current held constant the first order constant increases. Increase of temperature from 20 to 132° C. was required to cause the rate of decomposition to double. The rate also increases with increasing voltage. With initial hydrogen present with ammonia, the first-order velocity constant falls as the reaction proceeds; with initial nitrogen it rises. Equilibrium attained with ratio of nitrogen to hydrogen varying from 1:20 to 10:1 is not in quantitative agreement with the law of mass action, and is said to be independent of current and voltage, which is difficult to reconcile with the further statement that the rate of synthesis is faster the higher the voltage and current. There was some disagreement between Pohl (13) and Le Blanc (14) in regard to priority.

In a later and fuller account by Davies (15) it was brought out that the first-order rate of ammonia decomposition is maintained under constant current up to 80% of completion, after which it drops slightly. An increase of current of 30% causes an 80% increase in the rate of decomposition. The rate doubles on increasing the temperature through an interval of 100° C. The velocity constant increases slightly with decrease of pressure to 157 mm. at constant current. At constant voltage the increase of rate is greater for the same drop in pressure than with constant current. (This is obvious if one recalls that the current will rise if the pressure is lowered while the voltage is held constant.) Excess of hydrogen lowers, excess of nitrogen raises, the velocity constant at constant current. In synthesis most of the reaction occurs rapidly and then slows down; it increases with the current, increases slightly with excess of hydrogen and decreases slightly with excess of nitrogen. The equilibrium in a $3H_2:1N_2$ mixture, reached from both sides, is at 3% of ammonia by volume. The maximum ammonia content at equilibrium is also attained in stoichiometric mixture and is lowered by excess of either hydrogen or nitrogen, which again is difficult to reconcile with the statement just made about the relative rates with excess of one or the other. The equilibrium is independent of current and is not subject to the principle of mass action. Davies also thought that light from the discharge might play a role in the photochemical sense. (For discussion of this point see Warburg, [II, 2].)

In 1903 de Hemptinne (16) studied the rates of synthesis and decomposition of ammonia in point-to-plate discharge at 40-mm. pressure using a Ruhmkorff coil. In decomposition it made no difference whether the point was positive or negative. In synthesis the rate was slightly faster when the point was negative. No difference could be observed in rate with a static machine in reversing the poles.

Losanitsch (VII, 60) studied some addition reactions of ammonia with unsaturated hydrocarbons in silent discharge. Ethylene and ammonia gave an oily yellow liquid with strong odor and basic properties which was soluble in ether, benzene and acids but insoluble in water. Formula $C_{10}H_{21}N_3 = 183$; found 191 and 194. With acetylene an oily dark red liquid with strong odor and basic properties resulted which dissolved in alcohol and ether but not in water. Formula $C_{18}H_{30}N_4 = 302$; found 300 and 293. Benzene gave a basic, oily, reddish brown, strong-smelling substance, soluble in alcohol and ether. Formula $(C_8H_{12}N)_2 = 244$; found 254 and 251.

Comanducci (VIII, 39) found that a mixture of ammonia and oxygen in effluve gives traces of hydroxylamine, no hydrazine and no nitrous acid. Makowetzky (17) synthesized ammonia in glow discharge between an electrode in the gas phase and a liquid water surface. Besson (18) found that in silent discharge a mixture of hydrogen and ammonia besides showing decomposition of the ammonia also gave a little hydrazine. A mixture of ammonia and water vapor gave a test for hydroxylamine, which could not be obtained with oxygen and ammonia. But with excess of ammonia in oxygen one obtains both ammonium nitrite and nitrate.

Löb (VIII, 41), observed that a solution of ammonia in alcohol gives in silent discharge a mixture of hexamethylenetetramine and ammonium formate.

Briner (19) in a study of synthesis and equilibrium in the arc believed the reactions to be mainly thermal.

Briner and Baerfuss (20) made a further investigation of the best conditions of producing ammonia in the electric arc. The best yields with respect to energy or current were obtained with a $1N_2:3H_2$ mixture at atmospheric pressure, but at 100 mm. the most favorable mixture was $5N_2:1H_2$ (indicating that, though absolute density or "stopping power" plays a large role, there is also a mass-action factor which influences the rate). Platinum electrodes were found superior to iron or nickel. At low pressure the electrode separation made no difference. The best energy yield was 3.54 grams of ammonia per kilowatt-hour. At 10 mm. of the $5N_2:1H_2$ mixture the current yield is threefold that at atmospheric pressure. The iron or nickel electrodes which are inferior to palladium or platinum give the best yield at all pressures in the $3H_2:1N_2$ mixture. Moisture makes no difference in rate of synthesis. The arc is more effective than the silent discharge. No ammonia was produced in the separate action on either hydrogen or nitrogen, in accord with the results of Lewis in electrodeless discharge (XII, 90).

Warburg (21) compared the decomposition of ammonia by light and in electrical discharge. Later with Rump (22) he noted that ammonia synthesis occurs principally on the outer edge of the discharge region and suggested that it may be associated with a catalytic wall effect. They found the current yield to be much smaller in ammonia synthesis than in most other reactions. This is quite in accord with the low yield of ammonia in its synthesis under alpha radiation. Decrease of pressure affects the yield less than in synthesis of ozone.

Burk (23) studied the Stark effect in ammonia decomposition by examining its thermal rate at the heated surface of a molybdenum or platinum wire inside a copper cylinder. Fields of 44,000 volts per cm. for molybdenum and of 150,000 volts per cm. for platinum gave negative results, although the fields were within the range of a possible Stark effect.

Moens and Juliard (VII, 70) measured the synthesis of ammonia in silent discharge and found it to be faster in the presence of sulphuric acid.

Hutchison and Hinshelwood (24) compared the rates of decomposition of ammonia and of nitrous oxide in electrical discharge. Lind (25) showed that their results were those to be expected from the specific ionization and ion yield in the same two reactions under alpha radiation.

Goldstein (26) measured the rate of ammonia synthesis in an induction discharge at low gas pressure when the tube was partially immersed in liquid air. The clean-up of nitrogen by aluminum in the presence of argon was also described. The condensed discharge from a Leyden flask was more effective in this case.

Wendt and Snyder (27) found the equilibrium in corona discharge at 733 mm. and 28.5° C. to lie at 4.1% of ammonia by volume.

The formation of ammonia in the presence of mercury vapor at 10,000 volts and 50 cycles was studied by van der Wijk (28) at 45° and 100 mm. pressure. The reaction takes place at the mercury surface and is proportional to its extent. The following mechanism was proposed:

$$HgH_3 + N \rightarrow NH_3 + Hg$$

In silent discharge in the presence of mercury van der Wijk (29) found that the rate of synthesis varies as $-dx/dt = k \cdot H_2\sqrt{N_2}$ with a maximum rate for 67% H_2 and 33% N_2.

Employing direct-current discharge between metal plates, de Hemptinne (30) gives the data and calculation of the yield of ammonia molecules per electron of current shown in Table 19.

TABLE 19

YIELD OF AMMONIA MOLECULES PER ELECTRON OF CURRENT

A. de Hemptinne, Bul. sci. acad. roy. Belg. **14**, 450 (1928)

Time in minutes	Pressure in millimeters	$k \cdot 10^5$(amp.)	$N \cdot 10^{-15}$ (molecules NH_3)	$N'' \cdot 10^{-15}$ Ion pairs, calculated	$\frac{N''}{N}$
300	2.0	0.293	708	14,840	20
1100	2.0	0.029	310	5,500	17.8

Kunsman (31) compared the rates of clean-up of a $N_2 + 3H_2$ mixture at liquid-air temperature by electrons accelerated from a hot tungsten cathode and by K^+ ions from an iron potassium catalyst for ammonia synthesis. The electrons from tungsten showed the greatest activity above the ionization potential of nitrogen (17 volts). The activity of the iron-potassium surface is much greater than that of tungsten but is not enhanced by accelerating the K^+ ions.

Lavin and Bates (32) passed ammonia through a discharge tube and examined the reactions of the gases as evidence of the production of NH_2 or NH radicals. With ethylene, amines were formed; with oxygen, nitrides. Cupric oxide and ferric oxide extinguish the glow at once. Tin, copper, nickel, iron and platinum show induction effects. Molybdenum, tungsten and the $ZnO \cdot Cr_2O_3$ mixture showed little effect.

Rinkel (33) and Alsfeld and Wilhelmy (34) have studied the decomposition of ammonia in high-frequency glow discharge as dependent upon the presence of the decomposition products or excess of either. At pressures of a few millimeters (1.6–4 mm. initially) the rate of decomposition remains proportional to the partial pressure of ammonia up to 80% of completion. The rate for excess of nitrogen is greater than for excess of hydrogen (in accord with their relative stopping powers). The rate corresponds to first-order reaction. The maximum rate of synthesis is found by Rinkel et al. in a 1 : 1 mixture and by Alsfeld and Wilhelmy at 60% nitrogen. The equilibrium was found at about 2% ammonia. For synthesis the electrode materials increase in effectiveness as follows:

$$Al < Ta < Cu < Fe.$$

Brewer and Westhaver (IV, 41) used the glow discharge at pressures of 0.1 to 4 mm. to study the mechanism of ammonia synthesis. The distribution of the reaction in different regions of discharge was determined by quick removal and localization of ammonia by surrounding the discharge tube with liquid air. Most of the synthesis occurs in the negative glow, less in the positive column but uniformly distributed over its length. No synthesis takes place in the Crookes or Faraday dark spaces. Excess hydrogen diminishes the rate. Helium has no influence. Small amounts of nitrogen increase, larger amounts diminish, the rate. A mechanism is proposed based on the initiation of the synthesis by N^+ ions. Atoms, excited molecules and hydrogen ions ($H_2{}^+$) represent a loss of energy (page 16.)

Bredig, Koenig and Wagner (35) sought the best conditions for the formation of hydrazine from ammonia in the Siemens tube with either alternating- or direct-current discharge. The research was based on the hypothesis of the stepwise dissociation:

$$NH_3 \rightarrow NH_2 \rightarrow NH \rightarrow N$$

Both low and high pressures were employed as well as the cooled high-voltage arc. Low voltage and high rate of flow of ammonia were found favorable. The Schuster bands in the arc spectrum were found to be a good criterion of favorable conditions.

Koenig and Wagner (36) continuing the research proved the Siemens tube superior to the arc. With high rate of flow and low electrical intensity which decomposed 80% of the ammonia the exit gases contained 80% of hydrazine. The Schuster bands were gradually covered by a many-line spectrum as the decomposition of ammonia progressed. No Schumann bands are exhibited by hydrazine flowing through the discharge.

Schumb and Hunt (VII, 26) obtained the results shown in Table 20, for the synthesis of ammonia from a $3H_2:1N_2$ mixture in electrodeless discharge.

TABLE 20

AMMONIA SYNTHESIS IN ELECTRODELESS DISCHARGE

W. C. Schumb and H. Hunt, J. Phys. Chem. **34**, 1919 (1930)

	(1)	(2)	(3)	(4)	(5)	(6)
Initial pressure (mm.)	0.51	0.51	0.58	0.58	0.63	0.92
Final pressure (mm.)	0.47	0.435	0.53	0.495	0.535	0.78
Time (min.)	2	5	2	5	5	10
%NH_3	15.7	29.4	17.2	29.3	30.1	30.4

Numbers (2) and (4) in Table 20 were confirmed by Nessler reagent to within 2% of ammonia. Solutions containing 50 cc. of 0.05 *N* NH_4OH were obtained in half an hour. Equilibrium was attained with an ammonia content above the usual 3–4%. By ammonia decomposition at 0.64–0.92 mm. initial and 1.07–1.55 mm. final pressure, equilibrium at 67.5% of decomposition was reached in 2 min. Unpublished results with a vacuum-tube oscillator gave decomposition up to 100%.

Westhaver (37) studied the decomposition of ammonia in glow discharge. He discovered that some hydrazine is formed in the positive column but none in the negative glow. The rate is proportional to the current and independent of the pressure. The ions N_2^+, A^+, He^+, O_2^+ and Hg^+ initiate decomposition. H_2^+ does not. There is a small positive temperature coefficient above 250° but negative below 250°. The equilibrium mixture at room temperature contains about 6% of ammonia. The yield in molecules per ion is 0.5 to 1.0.

Schumb and Goldman (38) continued the investigation of ammonia synthesis in electrodeless discharge at pressures of 0.5 to 1.5 mm. of stoichiometric mixture with currents of 5.8 amp. Results were reproducible only after the vessel had been baked for an hour at 350° C. This indicated that synthesis under these conditions might be a wall reaction. This was confirmed by results with "packing" the reaction chamber. The authors propose the theory that active forms of nitrogen and hydrogen react at the wall to form ammonia, which in turn is adsorbed and stops further reaction when the wall is entirely covered with ammonia. The steady state is therefore conditioned by the rate of desorption of ammonia.

Koenig and Brings (39) measured the production of hydrazine by glow discharge in ammonia. Either the radical NH or NH_2 may be the intermediate product:

$$NH + NH_3 \rightarrow N_2H_4 \quad \text{or} \quad NH_2 + NH_2 \rightarrow N_2H_4$$

As much as 94% of the ammonia was converted into hydrazine at 4200 volts but only 60% at 14,500 volts.

The non-thermal ammonia equilibrium under influence of alpha radiation was experimentally determined by D'Olieslager and Jungers to be 4.7% of ammonia. It is interesting and to be expected that it has approximately the same value as those found by numerous authorities for the equilibrium in various types of electrical discharge. Lind (40) showed that the experimental value of D'Olieslager and Jungers is not given by the ratio of the rates of the two opposing reactions when the latter are measured beginning with pure ammonia or pure $3H_2 : 1N_2$ mixture, respectively, that is, far away from the equilibrium. This indicates that there must be an exchange of energy between the activated reactants and non-active products so as to shift the equilibrium in the direction of less ammonia. This would be the case if the ions with higher ionization potential H_2^+ (16 volts) and N_2^+ (17 volts) exchanged ionization with NH_3 (11 volts), assuming that the NH_3^+ ion produced would cause more decomposition than synthesis, which seems quite probable.

Jolibois (41) claims in a French patent that the synthesis of ammonia may be accomplished in glow discharge by introducing hydrogen and nitrogen into the cathodic region at pressures up to 50 mm. and with a current intensity sufficiently low to allow the electrodes to remain cold.

Makowetzky (17) passed glow discharge between a water phase containing some sulphuric acid to render it conducting and a gas phase containing oxygen or nitrogen or both at reduced pressure. Hydrogen and oxygen were formed in the gas phase when it was anode and a little ammonia in the water phase. When the liquid was made cathode it contained hydrogen peroxide and ammonia and nitric acid when nitrogen was present. The hydrogen peroxide exceeded the Faraday equivalence; 1000 coulombs suffice to produce one equivalent. But the sums of the reducing products and oxidizing products in the liquid phase were always equivalent to each other and corresponded to Faraday's law. Non-polar processes occurred in the gas phase only.

(1.8) Compounds of hydrogen and oxygen. The decomposition of water by direct-current electrolysis and the explosive union of hydrogen and oxygen by sparking have been known since the discovery of hydrogen. The phenomena which will be considered in this section are the decomposition of water or of water vapor by sparking or by other forms of discharge and the non-explosive synthesis of water from hydrogen and oxygen in silent and in glow discharge.

Decomposition of water vapor in the spark has been described by a number of early workers (42–45; VIII, 31; VIII, 33) most of whom also observed the slow recombination.

Perrot (3) found that a long spark produced more decomposition than a short one for the same current and correctly concluded that the decomposition is not due to ordinary galvanic (i.e., electrolytic) action.

There remained, however, much confusion in regard to this, and later Perrot himself thought that part of the action in induced direct current might be electrolytic when he found (3) that the action increases, though less than proportionately, with the length of spark, and that for a given apparatus there is an optimum spark length for maximum decomposition of water vapor. The question may be regarded as settled experimentally much later by the careful measurements of Lidbury and Chapman (46) of the decomposition of water vapor in the spark and comparison of the amount of hydrogen liberated in a voltameter in series which showed conclusively that the ordinary laws of electrolysis are not applicable. Lind (47) later showed that no connection should be expected between the current and the amount of chemical reaction in gaseous conduction, since the chemical change is dependent on the formation and recombination of ions which are usually far in excess of those that reach the electrode and cause the electrical conduction by their discharge. Holt and Hopkinson (48) showed that rate of diffusion also plays a large role in the separation of hydrogen and oxygen resulting from the decomposition of water vapor in the spark.

Berthelot (49; VII, 46, 52) compared the dissociation of water vapor and of carbon dioxide in the spark. He found similar behavior in decomposition and recombination. Excess of either hydrogen or oxygen in the case of water vapor causes complete combination and prevents decomposition. An equilibrium state could not be found.

The decomposition and synthesis of water in silent discharge has also been studied by many investigators. The Thenards (VIII, 37) were able to decompose water vapor in the effluve. They also found that, in the synthesis of ammonia, the presence of liquid water is not harmful but aids, as does concentrated sulphuric acid. Deherain and Maquenne (50) were also able to decompose water vapor in various types of ozonizers. They studied the conditions (51) for the explosion of hydrogen and oxygen in effluve. They found the presence of water on the wall favorable. In its absence only slow combination of H_2 and O_2 occurs until enough water forms on the wall for explosion to be initiated. In a later paper they attribute this to a condenser effect of the water on the wall which gives a more powerful discharge capable of decomposing water vapor and of causing nitrogen to combine with its decomposition products to form nitric acid (II, 4, page 376). De Hemptinne (16) found that in point-to-plate discharge in hydrogen and oxygen at 20–25 mm. pressure the reaction was faster when the point was charged negatively from a static machine but no difference was observed when charged from a Ruhmkorff coil.

Löb (VIII, 16) observed the decomposition of water vapor at 100° but not at ordinary temperature in silent discharge. He confirmed the slow synthesis. Smits and Aten (10) failed to decompose water vapor in an ozonizer and found that hydrogen and oxygen combined explosively.

In 1904 Kirkby (52) began a series of important studies of the slow combination of hydrogen and oxygen in direct-current glow discharge at low pressures (1–10 mm. of $2H_2 + O_2$). He found between 4 and 9 molecules of water formed for each ion pair discharged at the electrodes, which is in the region of 3–4 found by Lind (53) for alpha particles where no current passes and all the recombination is interionic in the gas phase. (See also later work by Brewer.) In a third paper Kirkby proposes that the primary action is the splitting of oxygen molecules into oxygen atoms by electronic bombardment, followed by the reaction $H_2 + O \rightarrow H_2O$, which theory he elaborated in 1911 (54). He found that the oxygen atoms are not charged, that the dissociation in the positive column is due to electron bombardment, that the rate of reaction is proportional to the current with a collision efficiency of 0.5 in the dissociation of oxygen. It appeared unnecessary to activate H_2. An equation was deduced for the synthesis of water:

in which p is the pressure in millimeters, y is the low voltage in glow discharge. However, Harteck and Kopsch (VI, 74, 91) found the reaction $O + H_2$ to be one of very low efficiency.

In 1908 Chattock and Tyndall (55) investigated the union of hydrogen and oxygen in unipolar point discharge in hydrogen at atmospheric pressure containing varying amounts of oxygen. Between 2 and 14% of oxygen, 16 molecules of oxygen reacted per ion (of current) with the point positively charged and 25 molecules of oxygen with the point negative. Below 2% oxygen, combination with negative point rose rapidly to attain the value 110 oxygen molecules per ion below 0.01% oxygen in hydrogen. For the positive point the oxygen reacting remains constant at 10 oxygen molecules per ion (of current) below 0.2% oxygen. Pressures of 1 volume of oxygen in 10^7 can be detected. When nitrogen is present with oxygen in hydrogen, even in enormous excess, combination is mainly and perhaps wholly between hydrogen and oxygen. The increase of oxygen in the mixture above 0.01% is thought to increase the size of the negative ion but not to affect the positive. In pure hydrogen a contraction of about 1 hydrogen molecule per ion of current was observed.

Hydrogen peroxide is often a by-product of the union of hydrogen and oxygen in electrical discharge. Fischer and Ringe (56) found traces of hydrogen peroxide on passing steam through a Siemens tube at 130°. A mixture of steam and oxygen gave better yields, of steam and air still better. Löb (VII, 57; VIII, 16) had previously reported the formation of hydrogen peroxide in silent discharge in the reaction between water vapor and carbon dioxide and carbon monoxide. Comanducci, (VIII, 39) failed to find any hydrogen peroxide formed in the union of hydrogen and oxygen in the ozonizer. Excess of hydrogen gave water only; excess of oxygen gave water and ozone.

Fischer and Wolf (57) succeeded in producing hydrogen peroxide in silent discharge through hydrogen and oxygen. Explosion was avoided by reducing the pressure, or by excess of either of the reactants or by introduction of a foreign gas such as carbon dioxide or argon. In equivalent mixture at 3-cm. pressure the yield was 2.25% hydrogen peroxide based on oxygen present. In excess (97%) of oxygen, ozone was formed. In excess (96%) of hydrogen, the yield of hydrogen peroxide at room temperature was 6.4%; at −20° C., 34%; at −80°, 54%; at liquid-air temperature, 60–87.5%. In a mixture of 4 parts of carbon monoxide, 2 parts hydrogen and 1 of oxygen a yield of 4% hydrogen peroxide, based on oxygen, was obtained. Wolf (58) in further refining the conditions for obtaining hydrogen peroxide found that high temperatures must be avoided. The pressure limit for explosion in his apparatus for silent discharge was 146 mm. of knallgas. The concentration limits for explosions in mixtures are 5.45% hydrogen or 5.3% oxygen. In knallgas at lower pressures the best yield obtained was 17%. In a mixture of 3% oxygen and 97% hydrogen, low temperature was very advantageous. At the optimum conditions, primary current 4.6 amp., gas flow of 0.4 liter per hour, with 8% hydrogen peroxide and 3.5% oxygen, a yield of 99.9 (based on oxygen) was obtained at −80° C.

Besson (59) employed the blue coloration of CrO_3 as a test for hydrogen peroxide (negative to ozone) in the decomposition of water vapor in effluve at temperatures several degrees below zero and pressures 30–760 mm. Water vapor alone gave no hydrogen peroxide. In water vapor and oxygen mixtures hydrogen peroxide was always found except at very low pressure and was especially strong in excess oxygen at 0.5–1 atmospheres. In air and water vapor the test was not strong. Besson suggests the formation of hydrogen peroxide by electrical discharge in the upper atmosphere.

Rodebush and Wahl (VI, 126) through a spectroscopic study of electrodeless discharge in water vapor found high yields of hydrogen peroxide and suggest homogeneous bimolecular combination of OH groups. New bands with heads at 3564 and 3328 Å appeared to be due to OH^+ ions. These bands were also found in condensed discharge between electrodes but not in the uncondensed. Geib (VI, 165) found that hydrogen peroxide is formed by discharge in water vapor both with and without electrodes at temperatures below $-100°$ C. He proposes a mechanism dependent on a third body X.

$$X + H \rightarrow XH;\ XH + O_2 \rightarrow XHO_2;\ XHO_2 + H \rightarrow X + H_2O_2$$

Bonhoeffer and Pearson (VI, 86) have proposed the following mechanism for the decomposition of water vapor in electrical discharge. $H_2O + (e) \rightarrow OH^* + H$. OH^* is excited with a life of 10^{-3} sec.

$$OH^* \rightarrow OH;\ OH + OH \rightarrow H_2O + O;\ O + O \rightarrow O_2;\ H + H \rightarrow H_2$$

Güntherschulze (60; I, 12) used the combination of knallgas in glow discharge to test his theory of chemical action in discharge as dependent on potential drop at an iron cathode. The straight line connecting the cathode drop of the two pure components in Fig. 7 is regarded as representing the normal cathode fall in any mixture. Departure from this, as in the case of hydrogen-oxygen which showed a large bend upward, represents the proportion of energy expended in the production of ions which enter into chemical action and do not take part in conduction. However, in the case of nitrogen-hydrogen mixtures the downward bend below the line indicates no tendency to reaction, which we know to be not entirely correct. (For further discussion and figures see Chapter I, page 14.)

De Hemptinne (30) employed direct-current discharge between plates at low pressures of 95% H_2 + 5% O_2 to obtain the results shown in Table 21, in which p is the initial pressure, i the current, N the number of water molecules formed, N'' the total number of ion (pairs) formed, as calculated by dividing the total potential drop V by the ionization potential of the gases. The calculated yields which would be the reciprocals of N''/N appear low. The method of calculating N'' (the ion pairs) is open to considerable question.

TABLE 21

WATER SYNTHESIS IN GLOW DISCHARGE

A. de Hemptinne, Bul. sci. acad. roy. Belg. **14**, 450 (1928)

Duration, min.	Pressure, mm.	$k \cdot 10^5$(amp.)	$N \cdot 10^{-15}$ (molecules H_2O)	$N'' \cdot 10^{-15}$ Calculated ion pairs	$\frac{N''}{N}$
30	1.66	0.183	364	920	2.5
60	1.57	0.012	117	211	1.8
10	1.54	0.72	175	900	5
30	2.70	0.146	200	560	2.8
60	0.22	0.083	38	120	3

The yield in water synthesis is seven to tenfold greater than that also found by de Hemptinne in synthesis of NH_3 from its elements under the same conditions.

In 1926 Finch and Cowen (61) made a study of the combustion of hydrogen and oxygen in direct-current glow discharge between metal electrodes 1 cm. long with conical tips. The rate of combustion is proportional to the current at varying electrode separation up to a current of 1 milliamp. The ratio of combustion to current is independent of voltage, pressure and electrode separation, but is dependent on the electrode material. Experiments with Cu-Pt and Pt-Cu "cathode-anode" material showed that combustion takes place in the cathode zone only. The combustion is not catalytic but a function of the electron emissivity of the cathode metal.

Above 1-milliamp. current the curves for combustion and current begin to run independently of each other when the pressure or distance between the electrodes is varied, the rate of combustion being higher for platinum than for copper cathode. At higher currents the combustion also extends into the interelectrode space and probably occurs in the positive column. Beyond a certain current density the combustion increases rapidly until ignition ensues. Both cathodic and interelectrodic combustion are proportional to the total number of ions formed in the discharge. For ignition a minimum concentration of ions is necessary, the accumulation of which may take a period of time as long as a few seconds, depending on the current and gas pressure. This critical concentration may occur first in the cathode or in the interelectrode space.

Later Finch and Cowen (62) investigated the current necessary to cause ignition of electrolytic gas in the same type of apparatus employing direct-current glow discharge. They found that ignition occurs immediately upon attainment of the minimum current, which is hyperbolically dependent upon the gas pressure, that is, the two are inversely proportional to each other, or their product $i \times P$ is constant. There is an optimum pressure of water vapor. The rate of flame propagation is at least 10 times faster along the path of electrical discharge. It was concluded by the authors that ignition is dependent on the attainment of a minimum concentration of ions in some portion of the gas, and that flame propagation is also essentially an electrical phenomenon.

The synthesis of water in electrodeless discharge has been the subject of investigations by Moens and Juliard (VII, 70) and by Rusk (63), who also employed the low-voltage arc. Rusk found more reaction with excess oxygen which he attributed, as Lind (53) had done in the reaction under alpha particles, to the greater stopping powers of oxygen—in this case, for electrons. Rusk concluded that the specific ionization of hydrogen and oxygen traversed by electrons is the same as that for alpha particles, a conclusion supported by the work of Lind and Glockler (VII, 72) and of Lind, Marks and Glockler (IV, 50) with the lower hydrocarbon gases of the saturated series.

In the extensive investigations of Brewer (I, 15) and his collaborators the synthesis of water in glow discharge has been the object of several of their studies. Metal electrodes, usually iron, were placed in glass vessels surrounded by liquid air, which had the advantages not only that the water formed was removed from the field of reaction but also, in some experiments, that the distribution of ice on the walls adjacent to the different portions of the discharge gave valuable indications as to the reaction mechanism. The current and voltage were carefully regulated and measured. Below 7.0-mm. pressure the reaction seemed to be initiated solely by H_2^+ ions. Accordingly the maximum rate in mixtures of varying proportions of hydrogen and oxygen was found far on the hydrogen-rich side—87% hydrogen, 13% oxygen at 3.5 mm. total pressure. Above 7 mm., O_2^+ ions also are effective as well as ions of foreign gases such as N_2^+ and A^+.

In the region of negative glow the ice deposited sharply and quantitatively on the neighboring wall, which was interpreted to mean that the synthesized water molecules reach the wall in the charged state. A more diffuse distribution in the positive column indicated that neutralization occurs both in the gas phase and at the wall. An ion-cluster mechanism with a yield $+M_{H_2O}$: electron (of current) = 4 (later revised to 2) is indicated in the negative glow; an ion-chain mechanism is suggested for the positive column. Ignition was found to start in the positive column only and to depend on both current density and gas pressure.

In investigating the influence of electrode material on the rates of synthesis of water and of ammonia, Kueck and Brewer (I, 18) found that reaction in the positive column is not affected by change of electrode material and they observed only a slight difference, up to 5%, in the negative glow upon changing the cathode in water synthesis. Greater differences were observed for ammonia. The metals used in water synthesis were aluminum, calcium, magnesium, zinc, cadmium, nickel, iron, antimony, tungsten, lead, and tin (page 14).

Chain reactions in the positive column in water synthesis were given special attention by Brewer and Kueck (64). A fixed aluminum cathode and a movable iron anode were placed in a 5-liter Pyrex glass cylinder which could be raised to any temperature up to 500° C. Marked differences were found to characterize the synthesis in the negative glow and in the positive column, which support the hypothesis of a chain mechanism in the latter. For example, the yield ($M_{H_2O}/H_2^+ = 2$) remains constant in the negative glow, whereas in the positive column it increases both with current and gas pressure until ignition takes place.

The addition of foreign gases increases the rate of reaction in the positive column, an effect opposite to that in the negative glow. The rate in the positive column is retarded by the proximity of walls and accelerated by temperature.

Since spectral evidence shows that free atoms and radicals, which would be expected to initiate and promote ordinary chain mechanism, abound in the negative glow only and are absent in the positive column, Brewer and Kueck dismiss the idea of their participation in the reaction and assume an ionic chain mechanism such as

$(H_2O_2)^+$
H_2O
H_2O

Such a mechanism is practically identical with that originally proposed by Mund (65) in the case of some alpha-ray reactions.

The temperature effect in the chain mechanism is generally expressed as

$$a = e^{-E/kT}$$

in which a is proportional to the probability of chain continuation, according to Semenoff (VI, 159), as dependent on the energy E resulting from the chemical reaction, and influenced by clustering of the ion center, and the collision of hot molecules with it, and on the temperature T.

The normal number of reaction centers in non-chain yield may be expressed as $w = n$, when n is the number of H_2^+ ions. Then in chain mechanism $w = n + wa = n/(1 - a)$, in which a is the probability of chain propagation.

The addition of water vapor up to 40% has no influence on the rate in the negative glow or in the positive column. This is interpreted as meaning that water molecule ions can also form reaction nuclei as found by Lind and Schiflett (66) for the same reaction under alpha radiation. Brewer and Kueck (67) observed that the equilibrium $2H_2 + O_2 \rightleftharpoons 2H_2O$ lies at 88% water vapor for both the negative glow and positive column.

A natural development of chain mechanism is its application to ignition, which Brewer and his associates have studied both in the condensed discharge (68) and in the positive column (69). The most easily ignited mixture in the positive column is one containing 25% H_2 and 75% O_2. A hyperbolic relation exists between the power input for ignition and the gas pressure. On increasing the absolute temperature from 300 to 600°, the ignitibility, inversely proportional to the necessary power input, increased ninefold. The ignitibility increases with the length of the positive column and is decreased by the presence of surfaces within 1 cm. of the discharge. Foreign gases raise the ignitibility in the positive column in proportion to their ability to retard diffusion, an effect exactly opposite to that in condensed discharge where the power input is increased in proportion to the energy absorbed by the foreign gas.

Although complete consideration of ignitibility is outside the scope of this work, some results of ignition in the spark (70) are of interest in which it was found that the energy of the spark Q is related to the critical pressure P by $P = Q\ (e^{(a/Q)} - 1)$ in which a is the activation energy. P was found to be lowered by carbon dioxide, nitrogen or excess of oxygen, but increased if the proportion of foreign gas exceeded 25%.

Carter and Campbell (71), using the low-voltage arc submerged in water between carbon or metal electrodes, produced carbon dioxide, carbon monoxide, hydrogen, graphitic acid, hydrated metal oxides from the metal electrodes, small amounts of saturated hydrocarbons and nitrogen. Dissociation into H and OH is assumed to account for at least part of the reaction. Hydrogen appeared to be 25% in excess of the total oxygen.

Linder (I, 8) in 1931 made a careful study of the decomposition of water vapor in glow discharge. He concluded with Brewer that the principal action occurs in the negative glow or in the adjacent Crookes dark space. He measured the amount of reaction by collecting the gases hydrogen and oxygen. The usual excess of hydrogen over oxygen was observed. Experiments were made at 0.75-mm. pressure with current from 1 to 28 milliamp. and electrode spacing from 1 to 9.75 cm. The net energy expended per molecule decomposed was a constant, 11 e.v. Although this is near the ionization potential of water vapor it was suggested from other considerations that the entire decomposition is not due to ionization but in part to excitation. The average electron energy found in the positive column, of only 3.71 e.v., shows that but little decomposition is to be expected in that region. Only 1 electron in 1000 would have even the excitation potential of 7.6 volts. (See also Chapter I, page 14.)

Yamaguchi (72) studied the decomposition of water at the surface of solutions of heavy metal salts using the arrangement frequently employed (14) of one electrode in the solution, the other in the gas phase, in this case a cathode above and metal anode in the electrolyte. The surface was covered with a layer of paraffin under which oxides, hydroxides and free particles of the heavy metal collected.

(1.9) **Hydrogen fluoride.** Berthelot (VII, 52) failed to find any sensible decomposition in spark discharge, although the glass walls were attacked by the hydrogen fluoride and a small amount of water was observed.

(1.14) **Hydrogen-silicon compounds.** Berthelot (73) found that silicon hydride (SiH_4) is readily decomposed in the spark to silicon and hydrogen.

(1.15) **Hydrogen-Phosphorus Compounds.** Buff and Hofmann (82, VII, 39) decomposed phosphine readily and completely both in the spark and in the arc.

P. and A. Thenard (VIII, 37) decomposed phosphine in silent discharge (effluve) but not completely. A liquid was first produced which later became amorphous. An addition product was formed in a mixture of phosphine and ethylene. The product contained at least one alkyl phosphide.

Berthelot (VII, 6, 48) found that phosphine in silent discharge undergoes the reaction:

$$2PH_3 \rightarrow P_2H_2 + 2H_2$$

In the spark (VII, 51) he found that it decomposes readily to hydrogen and a mixture of red and yellow phosphorus.

Smits and Aten (10) observed the ready synthesis and decomposition of phosphine in the ozonizer.

Kohlschütter and Frumkin (74) united hydrogen and phosphorus vapor in glow discharge to form solid compounds.

(1.16) **Hydrogen Sulphide.** Buff and Hofmann (82, VII, 39) confirmed an earlier observation of Davy that decomposition of hydrogen sulphide takes place readily and completely in the spark. Brillot (75) found decomposition of hydrogen sulphide in silent discharge (effluve), which was confirmed by Berthelot (VII, 48), who also found that hydrogen selenide behaved similarly. Much later Berthelot (VII, 52) found decomposition of hydrogen sulphide in the spark to be slow but complete.

Losanitsch (VII, 55) found that nitric oxide can oxidize hydrogen sulphide in the ozonizer.

$$2NO + H_2S \rightarrow H_2O + S + N_2$$

Smits and Aten (10) found hydrogen sulphide to be readily decomposed in the ozonizer. They also observed its synthesis, which, however, is much slower than the decomposition.

Glockler (VI, 41) proposed the theory that positive hydrogen ions, $^+$, act on solid sulphur owing to the formation of S^- ions by electron attachment. Lunt (VI, 47), however, showed that this suggestion does not accord with experimental observations.

Schwab and Seuferling (VI, 48), on passing electrolytic hydrogen through an ozonizer at 50-mm. pressure and then over solid sulphur (or arsenic), obtained a test for hydrogen sulphide (or arsenic hydride) about ten times as strong as the blank. This result has been questioned on the claim that the hydrogen sulphide may come from sulphur liberated by the effect of the discharge upon the glass wall. (See discussion under Active Hydrogen.) It may be doubted, however, whether the same argument can be sustained in respect to arsenic hydride.

Schwarz and Schenk (76) swept sulphur vapors through an ozonizer by means of a rapid current of argon. On mixing the sulphur-laden argon with hydrogen or carbon monoxide they found combination in the form of hydrogen sulphide or *COS*, respectively, which they attribute to some active type of the sulphur molecule. Dilatometric experiments gave no indication of dissociation of the S_2 molecule, and they therefore reject the idea that it may be S_3 or something similar to O_3. Schwarz and Kunzer (77) passed hydrogen sulphide through an ozonizer at different elevated temperatures. The higher the temperature the less the decomposition, owing to increased activation of sulphur vapor and the enhanced reverse reaction to form hydrogen sulphide. This is an interesting confirmation of the theory proposed by Lind (I, 7) to explain the negative temperature coefficient of the decomposition of hydrogen sulphide by alpha particles first observed by Wourtzel (78). The idea is simply that the increase of vapor pressure of sulphur with increasing temperature puts more sulphur molecules back into the vapor phase where they may be ionized by alpha particles or by electrons in electrical discharge. Truesdale and Lind (79) made an exhaustive study of the system hydrogen-sulphur-hydrogen sulphide under alpha radiation and obtained results in general agreement with the foregoing.

Schumb and Hunt (VII, 26) have demonstrated the synthesis of hydrogen sulphide in electrodeless discharge by spreading flowers of sulphur on the bottom of the discharge tube through which hydrogen was passed at 1.5 mm. and into lead acetate solution. A black precipitate of lead sulphide was obtained in 10 min.

(1.17) **Hydrogen chloride.** Attempts to decompose hydrogen chloride in the spark were made as early as 1800. Henry (80) in 1802 did not succeed except by the intermediation of oxygen either from air or water. Davy (81) obtained similar results.

Buff and Hofmann (82, VII, 39) also failed with the spark but decomposed it incompletely in the iron arc and observed that mercury became coated with mercurous chloride. However Sainte-Claire-Deville (2) succeeded in decomposing hydrogen chloride by the spark in the presence of mercury and also observed the formation of mercurous chloride. Berthelot (VII, 52) also found partial decomposition of hydrogen chloride in the spark.

Wiedemann and Schmidt (83) stated that the decomposition of gaseous hydrogen chloride and of the vapors of mercuric chloride, mercuric bromide and mercuric iodide does not obey Faraday's law.

In an ozonizer Moser and Isgarischew (II, 16) found no decomposition below 16,000 volts and could not observe the attainment of an equilibrium between decomposition and synthesis. The reaction between hydrogen chloride and oxygen they found to take place readily according to the Deacon equation

$$4HCl + O_2 \rightarrow 2H_2O + 2Cl_2$$

with a 95% yield of chlorine which amounted to 10–13 grams of chlorine per kilowatt-hour. Ozone was formed in the presence of chlorine.

Comanducci (VIII, 39), also using silent discharge, in mixtures of hydrogen chloride and oxygen gases, reported the production of Cl_2O and HClO as high as a 6.6% utilization of the hydrogen chloride.

Thomson (84) in 1895 claimed to have carried out the direct-current electrolysis of hydrogen chloride gas in a narrow tube ($HCl \rightarrow H^+ + Cl^-$) under such conditions that the decomposition products were transported to their respective electrodes, as shown by a red glow at the cathode and green at the anode.

The non-explosive synthesis of hydrogen chloride from its elements in silent discharge can be brought about as was shown by Fassbender (85), who pointed out the similarity to Jorissen and Ringer's (86) synthesis by means of radium which was also later the subject of experiments by Taylor (87), Bodenstein (88), Porter, Bardwell and Lind (89) and Lind and Livingston (90).

Günther and Cohn (XX, 5) ionized a stream of chlorine by means of point discharge which was then mixed with hydrogen. Both positive and negative ions were found to initiate the synthesis of hydrogen chloride. The yields were quantitatively equal for either charge, and lent themselves to mathematical treatment on a "cluster" theory.

Malinovskiĭ and Skruinnikov (91) have made an interesting investigation of the possibility of igniting a 1 : 1 gaseous mixture of hydrogen and chlorine by projecting into it high-velocity electrons (cathode rays) from a Coolidge tube delivering a current intensity of 0.6–1.0 milliamp. at 35–45 kv. into gas at pressures from 7.5 to 750 mm. In no case was ignition or explosion observed even when an ion concentration calculated to be 10^8 was attained. They estimated that a concentration 10^5 fold greater would be necessary. Without entering into the question of the minimum ion concentration necessary for detonation it may be stated that the results of Lind and his co-workers just cited showed clearly that the controlling factor for detonation by ions of a hydrogen-chlorine mixture is sensitivity of the mixture rather than concentration of ions produced in it. This follows from the fact that such a mixture containing radon does not explode at first but later has often done so after most of the radon had decayed owing to enhancing sensitivity having overtaken a diminishing ion concentration.

(1.34) **Hydrogen selenide.** The decomposition of hydrogen selenide has been observed by Berthelot (VII, 52) in spark discharge and in the ozonizer by Smits and Aten (10), who also found a weaker recombination of hydrogen and selenium.

(1.35) **Hydrogen bromide.** Berthelot (VII, 52) found hydrogen bromide to be decomposed in the spark, and Smits and Aten (10) observed its strong decomposition in flowing through an ozonizer.

(1.52) **Hydrogen-telluride.** Berthelot (VII, 52) decomposed hydrogen telluride readily in the spark. In fact, he found it so unstable that its tendency to spontaneous decomposition rendered its storage impossible.

(1.53) **Hydrogen iodide.** Berthelot (VII, 52) observed the decomposition of hydrogen iodide in the spark, and Smits and Aten (10) observed it in the ozonizer. Warburg (II, 10) studied the synthesis of hydrogen iodide in the ozonizer by passing a stream of hydrogen over solid iodine so as to obtain saturation at 19.6°, 30° and 40°, respectively, and then through the ozonizer, after which the yield of hydro gen iodide was chemically determined. He found that a steady state was attained under these conditions of about 9 moles of hydrogen iodide to 1 of iodine. The electrical yield was 3.3 to 9 molecules of hydrogen iodide per electron of current.

That this steady state is far from what one would expect in the absence of such a large excess of hydrogen is indicated by the results of Vandamme (92) and Mrs. Brattain (98) in alpha-ray synthesis when the decomposition yield is sixfold that of the synthesis in pure hydrogen iodide, and hydrogen and iodine, respectively, at the higher temperatures.

Indirectly the results of Lind and Livingston (XX, 10) in the alpha-ray synthesis and decomposition of hydrogen bromide also indicate that there would be a strong influence of hydrogen in shifting the equilibrium toward synthesis.

(2) **Fixation of helium.** Soon after the discovery of helium Berthelot (93) claimed to have effected its combination, as well as that of argon and nitrogen, with benzene and with carbon disulphide under the influence of the effluve in the presence of mercury.

With the growing knowledge of the extreme degree of chemical inertness of the rare gases fewer attempts were made to bring about their combination even under electrical influence.

In 1927 Morrison (94) passed helium and other gases at low pressure over a strong source of RaB and RaC simultaneously subjected to electrical discharge, then through U-tubes filled with glass wool, and then allowed them to impinge on a zinc sulphide screen. Oxygen and nitrogen gave no scintillations. Electrical discharge was necessary to activate hydrogen so that it gave scintillations. Helium also gave a positive though weaker effect. The hydrogen character of *o*-helium also suggested the possibility of forming helides of lead and bismuth.

Thomson (95) found no reaction between helium and phosphorus in electrodeless discharge.

Bruner and Bekier (96) found no change in the rate of decay of radon when exposed to electrical discharge in a mixture with helium, thus failing to show any reversal of the emission of helium as an alpha particle from radium. Naturally the modern theory of the nucleus and its energy barrier would account for this negative result.

Damianovich (97), passing electrical discharge between platinum electrodes in helium at low pressure, formed a product on the platinum electrode which decomposed on heating, leaving platinum, and which dissolved in aqua regia more rapidly than platinum or than products formed with platinum and oxygen, nitrogen or hydrogen under similar conditions of discharge.

(5.17) **Boron chloride.** Silent discharge in hydrogen reduces BCl_3 to boron with no indication of a subchloride (XIII, 44).

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CHAPTER X

CARBON COMPOUNDS CONTAINING NITROGEN, OXYGEN, SULPHUR AND HALOGENS (6 TO 6.17)

(6) **Carbon.** Since carbon vaporizes only at extremely high temperatures it cannot present a medium for ionization except in the arc or intense spark discharge. Although many interesting reactions have been found between carbon and other elements in the carbon arc, the electrical and thermal effects are so inextricably interwoven that they will not be considered.

(6.7) **Carbon-nitrogen compounds.** Cyanogen is exceptional in that its electrical synthesis was discovered before its decomposition. In 1859 Morren (IX, 4) synthesized it by passing nitrogen through the carbon spark. The following year Buff and Hofmann (VII, 39) found the decomposition of cyanogen to be complete and rapid in the arc but slow and partial in the spark. Its decomposition in the spark was also observed by Morren (XII, 3) and later by Berthelot (1), who previously had found that hydrogen (2) slowly acts on cyanogen in the spark to give a little acetylene.

In 1907 in one of the last of his long series of researches Berthelot (3) reported that no equilibrium is attained in the decomposition of cyanogen in the spark, the cyanogen disappearing completely. Hence he denied its synthesis under his conditions and rejected the application of the laws of thermodynamics.

The polymerization of cyanogen was first claimed by Berthelot (4) in the effluve, resulting in the rapid formation of paracyanogen. In 1901 he (VII, 52) confirmed the decomposition in the spark which is complete in dry gases.

Gaudechon (5) condensed cyanogen in the effluve to a solid with some elimination of nitrogen, varying, according to conditions, from $C_5N_{4.3}$ to $C_5N_{4.7}$.

In 1907 Berthelot (VII, 52) further observed the decomposition of cyanogen chloride ($C_2N_2Cl_2$) into its elements by sparking. Here again there was no equilibrium in the dry gases.

In 1930 Briner and Deshusses (6) failed to find any cyanogen formed in the arc or in effluve from either carbon and nitrogen, carbon monoxide and nitrogen or carbon monoxide and nitric oxide. They conclude that equilibria calculated by the Nernst heat theorem are not determining factors in electrical discharge, which liberates active atoms and radicals.

In the year following, Peters (7) circulated a mixture of 4 parts of carbon monoxide to 1 part of nitrogen through a discharge tube with steel electrodes at high current density. A yield of 0.1% of condensible product (cyanogen) was obtained on each passage. By continued circulation this could be built up to a 100% yield on a nitrogen basis.

(6.8) **Carbon-oxygen compounds.** The decomposition of carbon dioxide in electrical discharge is an often investigated and sometimes debated subject of research. As early as 1790 Morveau (8) attributed to Berthollet and Vandermonde the statement that on sparking carbon dioxide gas it increases in volume and becomes inflammable. The presence of water vapor was necessary for the latter.

Buff and Hofmann (VII, 39) cite Henry and Dalton as authorities for the imperfect decomposition of carbon dioxide by sparking. They state as a result of their own experiments that carbon dioxide is decomposed by the spark from an induction coil, rapidly at first with increase of volume, then more slowly until the accumulated mixture of carbon monoxide and oxygen explodes.

Perrot (IX, 3) obtained 200 cc. per hour of carbon monoxide and oxygen by streaming carbon dioxide past an induction spark. Boettger (9), however, claimed that carbon dioxide is not decomposed by the spark from a Ruhmkorff coil and observed that the electrodes must be placed nearer together than in hydrogen in order to secure discharge. Berthelot (VII, 37) stated that the two opposed reactions, decomposition and formation, do not lead to a definite equilibrium but one that drifts with change of the spark intensity. He placed the explosion limit at 18.6% carbon monoxide and 81.4% oxygen. He found that slow combustion could proceed to completion on either side of the explosive limit. However, he stated that in a stoichiometric mixture of carbon monoxide and oxygen equilibrium is attained. Further investigations (10) convinced him that carbon dioxide is readily decomposed by the spark until recombination begins, after which decomposition and formation alternate periodically in dominance. He had never observed the explosion of carbon monoxide-oxygen mixture in the decomposition of carbon dioxide as reported by Buff and Hofmann (VII, 39). Excess of either oxygen or carbon monoxide prevents the decomposition of carbon dioxide and likewise causes complete combination.

Thenard (11), using a Houzeau tube, studied the decomposition of carbon dioxide. He found that the oxygen formed becomes slightly ozonized but that most of the energy of the electrical discharge is imparted to the carbon dioxide. Brodie (12) also observed the decomposition of carbon dioxide when using it as an inert gas in ozone production by electrical discharge.

The decomposition of carbon monoxide in electrical discharge was not discovered as early as that of the dioxide. In 1860 Buff and Hofmann (VII, 39) reported that the spark has no chemical effect on dry carbon monoxide. In 1865 Morren (XII, 3) found that carbon monoxide in the spark undergoes the reaction: $2CO \rightarrow CO_2 + C$. The spectrum of carbon first appears which later gives way to that of carbon dioxide. Much later Berthelot (VII, 52) examined the same reaction in the spark and confirmed the reaction claimed by Morren but found it to be incomplete. Sainte-Claire-Deville (IX, 2) confirmed the decomposition in the spark of both carbon monoxide and carbon dioxide.

One of the earliest studies of the reactions of carbon monoxide with other gases besides oxygen was that of Berthelot (VII, 1), who in 1866 found that when a mixture of carbon monoxide and hydrogen is exposed to prolonged sparking in the absence of water vapor or carbon dioxide a little acetylene is formed.

In 1873 P. and A. Thenard (VII, 40) discovered the addition of methane and carbon dioxide in silent discharge (effluve) to produce a liquid which in time took on an amber color. The spark produced decomposition.

Also in 1873 Brodie (13; IV, 31) produced suboxide from carbon monoxide in silent discharge. He described the product as a dark brown solid soluble in water and ethyl alcohol, insoluble in ether — formula C_4O_3 and C_5O_4.

In 1876 Berthelot formed a brown suboxide of carbon from carbon monoxide in silent discharge (effluve) which he described as amorphous, extractable, very soluble in alcohol and in water in which it reacts acid, but insoluble in ether. The reaction he formulated as:

$$5CO \rightarrow CO_2 + C_4O_3$$

The suboxide on heating to 300°–400° underwent the reaction

$$3C_4O_3 \rightarrow 2CO_2 + 2CO + C_8O_3.$$

No mention was made of free carbon.

Schützenberger (14) employing effluve found a formula varying between the C_4O_3 of Brodie and the C_5O_4 of Berthelot. He further claimed some introduction of hydrogen which had come as water vapor through the wall of the tube under discharge and which caused some displacement of carbon monoxide from the suboxide giving compounds such as $C_{12}H_2O_{10}$ and $C_{12}H_2O_{11}$.

Berthelot (15) questioned the passage of water through the glass wall and disproved the claim of Schützenberger by new experiments. In reply Schützenberger (16) also performed further experiments which seemed to confirm his first results. In addition, he claimed that the condensation product of cyanogen may contain 1.5–2% of hydrogen and 8–10% of oxygen. Berthelot (17) advanced the argument that the water obtained by Schützenberger came from the large glass surface which he used and not through the glass. Schützenberger (18) adduced new evidence from the analysis of the condensation products of benzene and acetylene. In the former he found 1.2–7.0%, in the latter 16.1%, of oxygen. Further experiments with carbon monoxide (19) he regarded as supporting his contention.

In the light of modern research on the water content of glass and the difficulty of its removal either by baking or discharge it would appear that Berthelot had the more tenable view in claiming that water came from and not through the glass. This assumes, of course, that the analytical results were correct in showing its presence. Some doubt may be expressed also in that regard, since new evidence has been brought out as to the difficulties in analysis (VII, 66) and the ease with which some of these condensation products take on oxygen from the air (20).

In 1899 Berthelot began a series of researches on the reactions of the oxides of carbon in silent discharge. The reactions of carbon monoxide and dioxide with hydrogen have been described in (1.6.8). He found no reaction between nitrogen and carbon monoxide which undergoes its own reaction as if alone. The decomposition of carbon dioxide gave carbon monoxide, carbon suboxide and percarbonic acid (CO_3). In the presence of mercury no percarbonic acid formed, but carbon suboxide formed as in its absence. The decomposition of carbon dioxide (VII, 52) in the spark was confirmed.

Collie (21) showed far-reaching (65%) decomposition of carbon dioxide, in a spectrum tube, at a pressure of about 5 mm., whether wet or dry. Aluminum or platinum electrodes made no difference. Under the same conditions carbon monoxide proved much more stable. Electrodeless discharge in carbon dioxide also produced its decomposition up to 50%. In point-to-plate discharge de Hemptinne (IX, 16) found some tendency for decomposition when the point was negative, especially at low pressure (15 mm.).

Berthelot (22) in discussing the various types of suboxide put forward the hypothesis of an homologous series beginning with C and increasing by addition of CO radicals, C, C_2O, C_3O_2, C_4O_3, just as hydrocarbons increase chain length by CH_2 radicals. He referred to the work of Diels and Wolf, who obtained C_3O_2 by dehydrating malonic acid. Parenthetically, it may be mentioned that the polymerized form of the suboxide $(C_3O_2)_x$ obtained on the glass wall of vessels in which carbon monoxide is acted on by alpha rays is entirely inert to solvents including water, and shows no basic or acidic properties.

Fassbender (IX, 85) applied an electrical field to an explosive mixture of carbon monoxide and oxygen and found that it did not cause them to explode more readily upon sparking. The field did, however, cause their slow combination to take place more rapidly. A stronger field was required to affect the carbon monoxide-oxygen mixture than for a hydrogen-chlorine mixture. This is readily understood from the chain mechanism of the latter reaction which causes very high yields per ion pair. The explosion of carbon monoxide and oxygen produced a little ozone.

Holt (23), investigated the decomposition of carbon dioxide in ozonizer discharge. The dry gas is readily decomposed. The lower the pressure the greater the percentage of decomposition in the dry gas. The opposite is true in the wet gas. Smaller distance between the electrodes and more intense discharge both caused more decomposition. Discharge was passed until equilibrium was attained.

Moser and Isgarischew (II, 16) measured the equilibrium: $2CO_2 \leftrightharpoons 2CO + O_2$ in silent discharge. They found it to be easily reached from either side. Increase of voltage or current increases the dissociation. Increase of temperature or of electrode separation has the opposite effect. In excess of oxygen, ozonization disturbs the reaction. In excess of carbon monoxide, suboxide appears. The energy yield in the decomposition reaction is 1.2–6.3%. The current yield is 30–100 fold above Faraday equivalence. The presence of small amounts of chlorine greatly retards both the forward and back reactions.

Wendt and Farnsworth (24) studied the same equilibrium in corona discharge, which they reached in three-quarters of an hour at constant pressure. The decomposition attained 28.54% of the initial carbon dioxide, which would correspond to the thermal equilibrium at 2600° C.

According to Lōb (VIII, 41) a solution of carbon dioxide in water upon exposure to silent discharge gives tests for formaldehyde and ozone.

Ray and Anderegg (25) studied the oxidation of carbon monoxide by air or oxygen in the ozonizer. Small amounts of carbon monoxide in air or oxygen are not spontaneously oxidized by low concentrations of ozone unless the ozone is decomposed by special contact catalysts such as finely divided silver. Carbon monoxide is readily and almost completely oxidized by passing through the ozonizer with air or oxygen. The amount of oxidation may exceed the equivalent ozone obtained in the absence of carbon monoxide. It is suggested that active forms of carbon monoxide or of oxygen other than ozone are produced in the discharge. (Ions of both, of course, are present.) It is also possible that nascent ozone is accepted by carbon monoxide which otherwise would decompose.

Ott (26) observed that the suboxide (C_3O_2) formed from carbon monoxide in a Siemens tube may be precipitated as monoanilide by passing it into 5 cc. of aniline dissolved in 20 cc. of xylene. The ratio of products $C_3O_2 : CO_2$ corresponds to:

$$4CO \rightarrow C_3O_2 + CO_2$$

A yellow to brownish polymer is formed in the discharge tube and in the connections. No mention is made of free carbon.

Similarly to his experiments on hydrogen as a reducing agent toward metallic oxides in effluve, de Hemptinne (VII, 17; VIII, 43) tested carbon monoxide. Positive results were obtained with manganese dioxide, cupric oxide and a magnetic iron oxide. A comparative test showed carbon monoxide to be almost as effective as hydrogen in the reduction of lead dioxide.

Crespi and Lunt (27) have studied the formation of carbon suboxide in a Siemens tube of 250 cycles and 4500 and 9000 volts. They found the suboxide to be a hydroscopic solid with a ratio of carbon: oxygen increasing from 1.2 to 1.4 as the reaction proceeds. Carbon dioxide was also produced which accumulated until a constant ratio of 1 CO_2 : 12 CO was reached. Later Lunt and Venkateswaran (28) studied the same reaction employing a flow system in alternating corona of 20,000 volts and 250 cycles. Pressures were varied between 200 and 600 mm. The solid suboxide which was found to have the empirical formula $C_5O_3 \cdot xH_2O$ reacted with water with some liberation of carbon dioxide to form a brown solution, colloidal particles and a dark insoluble residue.

Jolibois, Lefebvre and Montagne (29) studied the decomposition of carbon dioxide using a discrete number (1–50) of condensed sparks at low pressure (0.3–20 mm.) from a source of 2400 volts with a condenser of 2.25 μf. Equilibrium representing 90% dissociation was produced in a 22-cm. tube by 20 sparks, with an energy yield of 20%.

The same authors studied the influence of varying the condenser capacity. Later the same authors compared the equivalent temperature for thermal dissociation of carbon dioxide and decomposition by sparking as a function of the capacity and gas pressure. For less than 0.1 μf the temperature is independent of the pressure; above 0.1 μf it is a complex function of pressure. They also determined the chemical yield in the decomposition of carbon dioxide at low pressures as a function of voltage, electrical capacity, pressure and shape of the tube.

In 1928 Jolibois, Lefebvre and Montagne (30) continued the study of the decomposition of carbon dioxide in the condensed spark and determined that with a capacity of 0.1 μf equilibrium was attained from both sides at 74% of decomposition of 25 mm. of original mixture. With continuous direct current in 9 mm. of initial carbon dioxide, equilibrium was reached at 33% of decomposition. For the same energy applied, constant low current is more effective than the high-capacity spark. With currents 0–0.002 amp. the dissociation of carbon dioxide at 3.4 mm. attains equilibrium at 42% of decomposition independent of the current, though it is more rapidly reached with higher current. The initial gas pressure affects equilibrium as follows: 0.8 mm., 54% decomposition; 1.9 mm., 48%; 3.4 mm., 44%; 5 mm., 40%; 8 mm., 31%. The energy yield decreases with increase of pressure from 4.8% at 0.8 mm. to 1.2% at 8 mm. for currents increasing from 100 to 900 microamperes.

Wendt and Evans (31) determined the equilibrium in corona discharge in the system: $2CO(37.1\%) + 2H_2(37.6\%) \rightleftharpoons CH_4\ (8.7\%) + CO_2\ (13.3\%)$ and found the values given in parentheses, which would correspond to a thermal equilibrium at about 900–950° C. This steady state in corona is only a temporary one as contraction of the gas volume continues and the final products, according to the authors, would probably be carbon and water. It appears that the reaction of a mixture of methane and carbon dioxide is quite different in corona from that in silent discharge where they combine to form a liquid (VII, 40) and again different from that under alpha radiation where they combine to a waxlike solid (IV, 51).

Guye and Luyet (32) measured the decomposition of carbon dioxide with a magnetic rotating electrode and found an equilibrium at about 90% of decomposition.

Taylor (33) discovered that, when oxygen enclosed in a glass tube is subjected to electrodeless discharge, carbon dioxide is condensed out at liquid-air temperature. The carbon must be derived from the glass vessel.

Finch and Hodge (34) treated a dry 2 : 1 mixture of carbon monoxide and oxygen with direct-current discharge between metal electrodes. They found that slow combination takes place near the cathode, which they believed to be due to the ions of both gases and to ions of the metal electrodes also. The rate of reaction was proportional to the current and independent of the pressure. Freely sputtering metal cathodes cause faster combination. When water vapor was introduced (35) by passing the mixture of carbon dioxide and oxygen through dilute sulphuric acid the rate of combination at the cathode of sputtering type is retarded though the rate remains independent of the total pressure. But at non-sputtering electrodes the rate is accelerated by the presence of water vapor, the influence of which is expressed by the equation $\left(\frac{c}{i} - 0.045\right) p = a$, in which c is the rate of combination of gas mixture in cubic centimeters per minute, i is the current in milliamperes, p the total pressure, and a is a constant dependent on the pressure of water vapor.

Lunt and Mumford (36) decomposed carbon monoxide in silent discharge. The reaction is not dependent on the presence of water vapor. Examination of the brown polymer of the suboxide C_3O_2 showed that it is not identical with polymerized malonic anhydride. Ott (37) was not able to accept this proof, but the evidence from the alpha-ray suboxide polymer (VIII, 23) supports the view of Lunt and Mumford.

Rheinboldt and Hessel (38) observed the formation of carbon dioxide in a high-frequency condenser at low gas pressures of 20–30 mm.

Peters and Küster (39) studied the equilibrium $CO_2 + H_2 \rightleftharpoons CO + H_2O$ at low pressures of 20–60 mm. in a discharge tube with water-cooled steel electrodes under several thousand volts. With increase of current the reaction rate rises until equilibrium is reached. Velocities of gas flow up to 710 liters per hour do not change the equilibrium. The yield is therefore directly proportional to the rate of gas flow. Equilibrium is reached in less than 0.15 sec. Temperature of discharge was 800–1000° C. In mixtures containing 25–100% carbon dioxide, the thermal equilibrium in the outflow gases calculated for 1200° K. corresponds to that found for constant load of 1.2 kw. For carbon-dioxide-rich mixtures equilibrium lags behind the temperatures. For pure carbon dioxide the equilibrium is above the observed temperature by 1000° C.

Among various solid substances examined in electrodeless discharge (40), carbonates and oxalates were found to be stable.

Employing high-frequency oscillatory electrodeless discharge, Hunt and Schumb (41) found that the equilibrium $2CO_2 \rightleftharpoons 2CO + O_2$ is established in 2 min. Equilibria at various pressures do not accord with the law of mass action. K_p is not constant but decreases with increasing equilibrium pressure. The presence of helium favors the decomposition of carbon dioxide. Excess of oxygen reduces the decomposition of carbon dioxide to a greater extent than carbon monoxide does, which is also contrary to the law of mass action.

Fischer, Küster and Peters (42) studied the decomposition of carbon dioxide between metal electrodes under various conditions. They confirmed the theory that the decomposition of wet gas is slower than that of dry gas, because of the accelerating effect of moisture on the reverse recombination. The rate of dissociation of dry gas was a maximum for a mixture containing 42% carbon dioxide at a total pressure of 40–60 mm., flowing at 100–150 liters per hour and at 2.0 kw. The rate increased sharply to the maximum with increasing pressure and flow and then fell linearly with further increase of flow. Greater current density increased dissociation. The energy efficiency was greater for faster flow. At 550 liters per hour the efficiency was 18%. The dissociation was interpreted as partly thermal, partly electrical. But little ozone was formed.

In 1934 Jolibois (43) compared the decomposition of carbon dioxide in the anode region (0.41%), in the positive column (3.2%) and in the cathode region (3.2%) of glow discharge, indicating much less reaction near the anode than in other portions of the discharge.

Lefebvre (VII, 100) showed in 1935 that the limiting yields of carbon monoxide and oxygen in the decomposition of carbon dioxide at low pressures by the condensed spark increase up to 2 mm. initial pressure and then remain constant to 25 mm. The limiting yield increases with the capacity of the spark condenser and may go above 95% if the initial pressure is only a few millimeters and the capacity a few microfarads.

Earlier, Brewer and Kueck (I, 17) had made a quantitative investigation of the non-explosive combination of carbon monoxide and oxygen in glow discharge. The rate is independent of pressure, proportional to the current, increases with excess carbon monoxide, decreases with excess oxygen almost in proportion to the excess. In the positive column the rate of combination is proportional to the current and independent of pressure up to 10 mm. At higher pressures the rate increases rapidly to ignition, which apparently starts only in the positive column. In the negative glow carbon dioxide reaches the wall in the charged state (CO_2^+), in the positive column as neutral molecules. Band spectra of carbon monoxide appear over a wide range of pressure. The authors interpret their data as indicating reaction through the intermediation of gas ions — ion clustering in the negative glow, chain reaction initiated by ions in the positive column which accounts for the onset of ignition there, but not in the negative glow. The ions of carbon monoxide (CO^+) were more effective than those of oxygen (O_2^+) in the positive column.

Finch (XX, 13) has given the following review of the work of himself and his collaborators, using metal electrodes.

(1) For dry carbon monoxide and oxygen:

$$2CO \rightarrow CO_2 + C$$

following which the carbon is burned by the oxygen.

(2) For dry $CO + O_2$ + metal (sputtered):

$$Me + O \rightarrow MeO \text{ (unstable)}; \quad MeO + CO \rightarrow CO_2 + Me$$

(3) Moist $CO + O_2$:

$$CO + H_2O \rightarrow CO_2 + H_2$$

(4) $CO + O_2 + H_2$: hydrogen burns via OH to water.

$$CO + OH \rightarrow CO_2 + H; \quad \text{also} \quad CO + H_2O \rightarrow CO_2 + H_2$$

(5) $H_2 + O_2 \rightarrow 2OH$, but if moist: $2H_2O \rightarrow 2OH + H_2$

OH is a very powerful promotor of oxidation.

(6) $H_2 + O_2 + Me$:

$$Me + O \rightarrow MeO; \quad MeO + H_2 \rightarrow H_2O + Me$$

(6.8.16) **Carbon-oxygen-sulphur compounds.** Berthelot (VII, 52) in 1901 found that carbonyl sulphide is decomposed by the electric spark into sulphur and carbon monoxide.

(6.8.17) **Carbon-oxygen-chlorine compounds.** Phosgene is decomposed in the electric spark to carbon monoxide and chlorine which attacks the mercury of the manometric system (VII, 52).

(6.9.17) **Carbon-fluorine-chlorine compounds.** Thornton, Burg and Schlesinger (44) found that dichlorodifluoromethane (CCl_2F_2) under action of high-tension (13,500 volts) discharge between copper electrodes (water-cooled) decomposes into chlorine, chlorotrifluoromethane (CF_3Cl) and small quantities of carbon tetrafluoride (CF_4), dichlorotetrafluoroethane ($C_2Cl_2F_4$) and some less volatile substances. Chlorotrifluoromethane also decomposes partially into carbon tetrafluoride, chlorine, dichlorodifluoromethane and small yields of less volatile products.

(6.16) **Carbon-Sulphur compounds.** In 1866 Berthelot (2) found that hydrogen and carbon bisulphide react in the electric spark to produce some acetylene and free sulphur.

Soon after the discovery of argon, Berthelot performed experiments to test its ability to form compounds with different substances in electrical discharge. He claimed the combination of argon and carbon bisulphide in silent discharge (45) and soon thereafter made a similar claim for helium and carbon bisulphide. Between nitrogen and carbon bisulphide he found combination (46) in both the spark and silent discharge.

In 1897 de Hemptinne (47) using oscillatory discharge in the decomposition of carbon bisulphide found that the rate was correctly expressed by a first-order kinetic equation. A few years later (IX, 16) he showed that in point-to-plate discharge in carbon bisulphide at 23-mm. pressure the rate of decomposition to sulphur and carbon is the same whether the point be charged negative or positive.

In 1900 Berthelot (48) exposed mixtures of carbon bisulphide and various gases to silent discharge. Hydrogen and carbon bisulphide condensed in the ratio $2CS_2 : 1H_2$. In a mixture containing originally $100H_2 : 133CS_2 : 81A$, the condensed product consisted of $77CS_2 : 38H_2 : 2A$. In the complete condensation of 69 volumes of carbon bisulphide at 12.6 volts in a mixture with 100 volumes of nitrogen only 16 volumes of nitrogen condensed or about $4CS_2 : 1N_2$. But at 25 volts the ratio was $7CS_2 : 1N_2$. For mixtures of 100 volumes of argon and 70 volumes of carbon bisulphide at 6.3 volts for 3 hours the condensation was $70CS_2 : 2A$; at 12.6 volts for 5 hours no argon was carried down though the carbon bisulphide was completely condensed; at 4.2 volts for 6 hours 72 volumes of carbon bisulphide in complete condensation carried down 3 volumes of argon. The lack of constancy indicates an absorption or co-precipitation of argon rather than a real combination of argon. A mixture of $60CS_2 : 100CO$ at 6.3 volts in 10 hours condensed almost completely (except 3.5CO) to a yellow solid mixture of addition products which on treatment with water yielded an acid containing sulphur and oxygen. On sparking a mixture of carbon bisulphide and nitrogen Berthelot (VII, 52) obtained only free sulphur and carbon. (The voltages given were applied to the primary of an induction coil.)

Losanitsch (VII, 55) tested the reactivity of carbon bisulphide toward various gases in silent discharge. Carbon bisulphide alone condensed to a dark brown polymer. With hydrogen or hydrogen sulphide a brown insoluble solid ($3CS_2 \cdot H_2$) was produced; with carbon monoxide a brown insoluble solid mass ($3CS_2 \cdot 2CO$); with ethylene a brownish yellow solid ($5CS_2 \cdot 2C_2H_4$); and with acetylene a black insoluble solid ($3CS_2 \cdot 2C_2H_2$). At very low pressure (VII, 63) carbon bisulphide gave the same result as at atmospheric pressure.

In glow discharge at 1-mm. pressure Dewar and Jones (49) found the following reactions:

a brown solid which forms from CS with explosive violence.

Moens and Juliard (VII, 70) attempted to decompose or polymerize carbon bisulphide in electrodeless discharge. Discharge, which could not be established above 1-mm. pressure, failed to produce any detectable change of pressure in the gas.

Emi (50) passed carbon bisulphide at 0.08 mm. through electrodeless discharge of 10^7 cycles at 2000–3000 volts and obtained a dark brown solid, apparently a polymer of CS, with an indication of $(C_3S_2)_x$ also. No evidence was obtained for the existence of a stable gas CS.

(6.17) **Carbon-chlorine compounds.** The decomposition of carbon tetrachloride has been observed in the high-tension arc by Schall (51); in electrodeless discharge at 1-mm.pressure by Moens and Juliard (VII, 70); and in high-frequency glow discharge by Hiedemann (VIII, 26). Schall also found perchlorobenzene, phosgene and hexachloroethane in small quantity.

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CHAPTER XI

NITROGEN COMPOUNDS WITH OXYGEN, PHOSPHORUS AND HALOGENS (7 TO 7.15)

(7) **Nitrogen (electrical fixation).** The present section deals with the electrical fixation of nitrogen, exclusive of the oxides of nitrogen (7.8), ammonia which has already been treated (1.7) and the so-called *active nitrogen* of Strutt and his followers, which is treated in Chapter XII.

In 1869 Berthelot (VIII, 1) stated, what he reaffirmed in 1901 (VII, 8), that the sparking of pure nitrogen does not render it able subsequently to combine with hydrogen or with acetylene. Later (VIII, 2) he found that nitrogen exposed to silent discharge (effluve) over benzene is absorbed at the rate of 4–5 cc. per gram of benzene in a few hours. The reaction occurs in the gas phase or in the liquid layer on the glass wall above the liquid. A resinous solid was formed which yielded ammonia on strong heating, but gave no ammonia without heating. A little acetylene was formed in the gas phase, as always in hydrocarbons in the effluve. Turpentine reacts like benzene but more slowly. In a mixture of nitrogen and acetylene the principal reaction is polymerization of acetylene (as in the alpha-ray reaction). No hydrogen cyanide is formed, which is abundant in the spark, but the solid polymer on strong heating gives a little ammonia.

Berthelot (VII, 6 and 48) succeeded in fixing nitrogen in moistened filter paper and obtained ammonia by heating it strongly with soda lime. Oxygen (air) does not interfere. A syrupy solution of dextrin also absorbed nitrogen. Berthelot believed the absorption to be a direct chemical one without first passing through ammonia or oxides of nitrogen as intermediate products. Berthelot found that the electrical fixation of nitrogen on organic matter by atmospheric electricity is quite general; he demonstrated it on a laboratory scale with primary voltages (32–132) volts) from Leclanché cells. He showed the fixation of nitrogen in the effluve by carbon bisulphide (X, 46) and by benzene (1), in which a compound was formed in the proportions $3C_6H_6:N_2$.

The reactions of nitrogen with mixtures of hydrogen and the oxides of carbon have been described in (1.6.8 and 6.8).

In a series of experiments on the activation of nitrogen Lowry (2) affirmed that the spark renders nitrogen capable of being oxidized by ozone to form nitrogen dioxide. He used in series the ozonizer followed by the spark or the spark followed by the ozonizer. Both gave the spectrum of nitrogen dioxide, stronger in the order ozonizer → spark. Seventeen sparks in series gave nitrogen dioxide slowly because there was time for the reaction to occur:

$$NO + O \rightarrow NO_2$$

Lowry affirmed the activation to be due to the formation of nitrogen ions or atoms which could react with ozone.

Koenig and Elöd (XII, 37) found that activation of nitrogen and oxygen takes place in the direct current glow so that they are capable of interacting outside of the field. They cite Strutt as having shown that active nitrogen decays more slowly than nitrogen ions recombine.

Koenig (XII, 45) confirmed Strutt's results on the activity of nitrogen produced in low-pressure discharge. Afterglow occurs at low pressure even when chemical activity is absent. The afterglow is unfavorably influenced by metal vapors and dust. Oxygen helps the afterglow by oxidizing metals that would otherwise form nitrides which would inhibit it. Direct-current glow discharge is equally effective with the condensed spark in giving nitrogen that is active toward ethylene, acetylene, pentane, nitric oxide and metals but not toward hydrogen, methane, oxygen or ozone.

De Hemptinne (VIII, 43) found nitrogen in silent discharge to have no effect on lead dioxide.

Moldenhauer and Möttig (3) studied the action of nitrogen in the electric spark between metal electrodes on the alkali metals. Cesium, rubidium, potassium and sodium form azides, and by secondary action small quantities of nitrides of cesium, rubidium and potassium. Lithium gave no azide but a little nitride. They assert that the claims of previous authors (4) to the primary formation of nitrides of alkali metals in electrical discharge are erroneous.

Moldenhauer and Dörsam (5) found that electrical discharge between aluminum plates at reduced pressure (below 200 mm.) in nitrogen and vapors of phosphorus gave the nitride PN, which on heating with concentrated sulphuric acid proved to be more stable than the nitride P_3N_5 which is formed in incandescent light bulbs when phosphorus is employed to fix residual traces of oxygen and nitrogen (XIII, 29). Using a similar apparatus for discharge between aluminum electrodes (at 80–100° C) Moldenhauer and Zimmerman (6) showed that nitrogen combines with sulphur vapor to form several sulphides, N_2S_5 (10%), N_2S_4 (75%), and NS_2 (15%) or $(NS_2)_x$.

The activity of nitrogen in electrodeless discharge has also been demonstrated with magnesium to form magnesium nitride by Schumb and Hunt (VII, 26), the rapid combination with phosphorus to form the nitride by Thomson (IX, 95).

Newman (VII, 12, 13) demonstrated the absorption of nitrogen by mercury, cadmium, antimony, bismuth, magnesium, calcium, zinc, tin, phosphorus, sulphur and iodine when these elements are deposited on the cathode in electrical discharge through nitrogen. Phosphorus, sulphur and iodine absorbed nitrogen in large amounts and were also the only ones that absorbed hydrogen under the same conditions. Neither nitrogen nor hydrogen was absorbed by lead, thallium or arsenic. Sodium, potassium and sodium-potassium alloy also absorbed nitrogen. The presence of nitrides was shown chemically for sodium, potassium, magnesium and tin.

Willey (XX, 16) found that the controlled impulse discharge of a condenser is superior to alternating- or direct-current discharge in the production of active nitrogen. Concentrations up to 40% of active nitrogen were obtained in the production of nitric oxide or 13% in the formation of hydrogen cyanide from the reaction of active nitrogen with organic vapors. The yields were proportional to the power input.

(7.8) **Nitrogen-oxygen compounds.** Lavoisier (7) in his Memoirs (Vol. 2, page 211) mentions the use of the electric spark to cause nitrogen and oxygen to combine, a suggestion which he attributed to Seguin which is also cited by Longchamp (8).

In 1859 Perrot (9) distinguished between the immediate combination of hydrogen and oxygen in the spark and the slow combination of nitrogen and oxygen. He found the latter faster in a long than in a short spark.

Buff and Hofmann (VII, 39) decomposed nitrous oxide in the spark to the elements which later recombined under continued discharge to an oxide with reddish color accompanied by some fixation of oxygen by mercury, which had also been studied by Gay-Lussac, the Thenards and Davy (VII, 39).

Buff and Hofmann also decomposed nitric oxide slowly in the spark. Red vapors were formed in the early stages. Mercury became tarnished, and the gas volume was finally reduced to one-half, the residue being nitrogen. A small amount of nitrogen was also taken up by the mercury. Priestley had earlier studied this reaction. In the same paper Buff and Hofmann describe the production of red vapors by sparking air, which reddens litmus in a few seconds. The presence of water vapor greatly facilitates the reaction. The same reaction had earlier been discovered by Cavendish (10), and referred to by Becquerel and by Boettger (11).

Berthelot (12) made a further study of the decomposition of nitrous oxide in the spark. He claimed that the decomposition to the elements is principally attributable to the thermal action of the spark, but that both thermal and electrical influences are involved in the accompanying reaction:

$$4N_2O \rightarrow 2NO_2 + 3N_2$$

He cites the work of Priestley, Grove, and Andrews and Tait.

In 1873 P. and A. Thenard (VIII, 37) observed the combination of nitrogen and water vapor in effluve probably to form ammonium nitrite.

In silent discharge Berthelot (X, 4) showed that nitrous oxide is decomposed to the elements accompanied by fixation of oxygen by mercury but not by fixation of any oxides of nitrogen by mercury.

Berthelot also investigated the decomposition of nitric oxide. In the spark he claimed two simultaneous reactions:

$$4NO \rightarrow N_2O + N_2O_3\ (\tfrac{1}{3});\quad 4NO \rightarrow N_2 + 2NO_2\ (\tfrac{2}{3})$$

After 1 hour no nitrous oxide (N_2O) remains. After 18 hours the residual gas contains 44% N_2, 37% O_2 and 13% NO_2.

In silent discharge nitric oxide is decomposed to nitrogen, oxygen and nitrous oxide, accompanied by the spontaneous combination of nitric oxide and oxygen to form nitrogen dioxide which is fixed by the mercury.

Later Berthelot (13) found that mixtures of nitric oxide with certain combustible gases will not inflame on being sparked while others will, which he attributes to higher heat of reaction in the latter cases.

In the spark Berthelot (12) found that nitrogen dioxide is decomposed into the elements to reach an equilibrium between 28% N_2, 56% O_2 and 14% NO_2.

In 1881 Berthelot (14) observed that mixtures of nitrous anhydride (N_2O_3) and oxygen unite in effluve to form a higher oxide which is not the pentoxide (N_2O_5) and which on standing becomes colored by the formation of the dioxide. About the same time Hautefeuille and Chappuis (15) found spectrally that under certain conditions in the effluve pernitric acid is formed even when nitrous anhydride is not. The upper temperature limit for the formation of pernitric acid is 130° C. Water vapor favors the production of nitric acid.

Continuing his investigation of the electrical synthesis of the oxides of nitrogen, Berthelot (VII, 52) showed that the presence of nitrogen dioxide formed in the spark by the addition of oxygen to nitrogen could be detected by its reddish color and by the bright pink color produced in a solution of ferrous sulphate in sulphuric acid when introduced into the gases containing nitrogen dioxide. The decomposition of nitrous oxide and of nitrogen dioxide by the spark was also observed.

In one of his last researches Berthelot (16) studied the union of nitrogen and oxygen in the effluve in the presence of water or sodium hydroxide in static and in flow systems. No difference was noticed between the influence of water and that of sodium hydroxide solution. Oxygen is pronounced the active agent whether in excess of nitrogen or not. Nitric acid is the exclusive product, even in excess of nitrogen, because ozone which is always present oxidizes nitrous to nitric acid while nitrogen cannot reduce nitric acid. An electrical condenser had no influence on the reaction rate. The rate increases with reduced pressure. The reaction: $N_2 + \frac{5}{2}O_2 + H_2O \rightarrow 2HNO_3$ is exothermic; the reaction: $N_2 + O_2 \rightarrow 2NO$ is endothermic at all lower temperatures. (The low energy yield of the reaction is in accord with its probable ionic mechanism in both reactions.)

On combining nitrogen and oxygen by sparking over potassium hydroxide in the purification of argon, Berthelot (X, 48) observed that the ratio of oxygen to nitrogen combining is considerably less than *two*, showing that some nitrous anhydride (N_2O_3) is directly formed and absorbed as nitrite without oxidation to nitrate. Briner and Durand (17), employing the same method they had used for synthesis of ammonia—sparking and condensation by carbon dioxide snow or liquid air—measured the synthesis of nitrogen dioxide as a function of the pressure and the percentage mixture. The best mixture was 1:1. The maximum yields were obtained in the range 4–145 mm. At 100-mm. pressure the yield reached 1.49 grams of nitric oxide (NO) per kilowatt-hour, which exceeded the yield attained in ammonia synthesis. There was some evidence for the formation of nitrous anhydride by escape of oxidation to nitrogen dioxide. (See above.)

Warburg and Leithäuser (18) made a series of investigations of the union of nitrogen and oxygen in ozonizer and in brush discharge. In the presence of ozone, nitrous gases are readily absorbed by sodium hydroxide solution. In still and brush discharge in air at room temperature 10 liters of nitric oxide were produced per ampere-hour independent of the moisture content. The amount of oxide formation increases with temperature until ozone decomposition becomes too great. Nitrogen tetroxide (N_2O_4) corresponding to 1 cc. of nitric oxide in 1500 cc. prevents the formation of ozone in air by brush discharge. In ozonizer discharge in air the chief product is nitrogen pentoxide (N_2O_5), part of which in the presence of ozone is transformed to an oxide (probably identical with the peroxide N_2O_6 of Hautefeuille and Chappuis (15)), which could not be found in the absence of ozone, and which always remains small in proportion to the pentoxide. The authors, however, hold that the formula N_2O_6 is not justified. The presence of the higher oxide can be recognized by its absorption spectrum in the visible region.

Losanitsch (VII, 55) studied some reactions of nitrogen and nitric oxide in silent discharge. He asserts the principal reaction of the latter to be:

$$4NO \rightarrow N_2O_4 + N_2$$

He found that nitric oxide is reduced by hydrogen:

$$2NO + 2H_2 \rightarrow 2H_2O + N_2$$

but accompanied by a little ammonia and nitrous acid. He confirmed the reaction:

$$2H_2O + N_2 \rightarrow NH_4NO_2$$

He found that nitrogen and hydrogen sulphide interact to form ammonium polysulphide:

$$N_2 + 4H_2S \rightarrow (NH_4)_2S_4$$

The reaction: $2NO + 2H_2S \rightarrow 2H_2O + S_2 + N_2$ is cited in (1.16).

Manchot (19) confirmed the presence of oxides of nitrogen in the ozonization of oxygen containing only 1–2% of nitrogen. He could find no acid reaction of ozone after removal of oxides of nitrogen.

Brion (20) has discussed the nature of the synthesis of oxides of nitrogen in electrical discharge. He concludes that with high temperature and high current densities the thermal influence controls the reactions. For low current densities and low temperature, both thermal and electrical influences are exerted.

Löb (21) asserts as the result of his experiments in silent discharge that neither in moist nitrogen nor in moist nitric oxide is there any formation of ammonium nitrite by direct action of water vapor. Water must be dissociated, and ammonia and nitric oxide are then formed by independent mechanisms.

In 1908 Cramp and Hoyle (22) gave a comprehensive review of yields of nitric oxide and nitrogen dioxide in glow discharge, spark, nitrogen flame, high-tension flame and arc discharge under various conditions.

Again employing the method of sparking the gas mixture and cooling the wall of the reaction chamber Briner and Durand (VIII, 8) made further investigations of the synthesis of nitrogen dioxide. The maximum yield attained in air at 15° is 5–6% of the oxygen combined; at $-78°$, 12–15%; at $-192°$, 20% or almost complete combination. In a mixture of $1N_2:2O_2$ almost complete vacuum is attained by sparking at liquid-air temperature. But the best power yield is obtained in a 1 : 1 mixture at 50–150 mm. pressure with a production of 0.77 gram of nitrogen dioxide per kilowatt-hour.

Makowetzky (IX, 17) demonstrated the formation of nitric acid in glow discharge between a gas phase of nitrogen and liquid water.

Zenneck and Strasser (23) examined the decomposition of nitrogen dioxide in glow discharge and found that it appears to take place in steps:

$$NO_2 \rightarrow N_2O_3 \rightarrow NO \rightarrow N + O$$

This was confirmed by spectroscopic evidence obtained at different stages in a flow system.

Ehrlich and Russ (24) made an extensive investigation of the formation of nitric oxide, nitrogen pentoxide and ozone in mixtures of nitrogen and oxygen in electrical discharge in a Siemens tube. In excess of ozone they found the reactions:

$$N_2 + O_2 \rightarrow 2NO; \quad 2NO + O_3 \rightarrow N_2O_5$$

In the absence of ozone the pentoxide decomposes to oxygen and nitrogen dioxide, which in turn is decomposed almost completely until an equilibrium is reached with nitric oxide. The inhibition of ozone formation by small amounts of nitrogen dioxide is connected with this equilibrium but independent of the initial ratio of nitrogen to oxygen.

Müller (25) produced ozone by passing electric sparks through liquid air and also obtained a green solid with the formula N_2O_3 which turned blue upon exposure to light. Possibly the peroxide NO_3 is first formed by sparking.

Contributions to the question as to whether it is necessary to activate both nitrogen and oxygen or only oxygen in order to cause their union in electrical discharge have been made by Fischer (26), by Fischer and Hene (27), by Koenig (28), by Koenig and Elöd (29) and by Tiede and Domcke (XII, 28) (see also Chapter XII).

In his theory of this reaction, Strong (30) was one of the first to propose an ionic theory of chemical action in electrical discharge.

Koenig (VII, 9) found that active oxygen in the afterglow produced nitric oxide at ordinary temperature by combination with active nitrogen.

Briner (IX, 19) concluded that the formation of nitric oxide in the arc is mainly thermal.

Ehrlich and Russ (31) tested the influence of ozone and nitrogen pentoxide on discharge through air in the Siemens tube. Both of them increase the arcing potential in mixtures of nitrogen and oxygen.

Harding and McEachron (32) studied the possibility of developing a commercial method of making nitric oxide from air in silent discharge. The maximum yield of 5.55 grams per kilowatt-hour is much below that of the arc process. (See also Hugo Spiel's Thesis, Techn. Hochschule,., Vienna, 1909.)

Joshi (33) studied the decomposition of nitrous oxide (N_2O) in silent discharge 6–12.5 kv. at pressures 110–820 mm. The reaction rate was slower the higher the pressure and the lower the voltage. He believed that the two simultaneous reactions:

$$2N_2O \rightarrow 2N_2 + O_2 \quad \text{and} \quad 2N_2O \rightarrow 2NO + N_2$$

and the intermediate reaction:

$$2NO + O_2 \rightarrow 2NO_2$$

all lead to complete decomposition to the elements.

Hutchison and Hinshelwood (IX, 24) measured the relative rates of the decompositions of ammonia and of nitrous oxide under similar conditions of discharge in the two cases. The decomposition of nitrous oxide was found to be several times faster than that of ammonia, a result not to be expected on thermodynamic grounds. Lind (IX, 25) reconciled and correlated the results with gaseous ionization on the assumption that their relative specific ionizations and chemical yields per ion would be the same in electrical discharge as in the same reactions under alpha radiation.

Briner and Rivier (34) found that discharge between metals which furnish most electrons at the lowest ionization potentials show the greatest efficiency in the formation of oxides of nitrogen from the elements. Addition of alkaline earth and rare earth oxides to the metal electrodes increased the yield in the order of their atomic numbers.

Westhaver and Brewer (I, 16) measured the combination of nitrogen and oxygen in glow discharge. In a mixture of 2 volumes of oxygen to 1 of nitrogen the formation of nitrogen dioxide is proportional to the current and independent of pressure in the range used (0.07–4 mm.). Argon and excess of oxygen decrease the rate; nitrogen accelerates it. Helium has no effect. The optimum mixture is 40% O_2 – 60% N_2. The yield was estimated to be one molecule of nitrogen dioxide formed for each electron flowing.

Laporte (35) determined the synthesis of nitric oxide by high-frequency silent discharge in air with mixtures of nitrogen saturated with water vapor. Frequencies exceeding 500,000 cycles were employed to prevent the neutralization of positive or negative ions at the electrodes. The optimum mixture contained 3% of oxygen. Water vapor is advantageous. Excess of nitrogen was claimed to be favorable because the electrons require only a small proportion of oxygen molecules to form negative ions. (Although oxygen has a great affinity for electrons, the claim made is not obvious.) No quantitative yields are given. The reaction is assumed: $N^+ + O^- \rightarrow NO$, which neglects the problem of dissipating the large energy of recombination of the ions.

Kueck and Brewer (I, 18) studied the decomposition of nitrous oxide in glow discharge. The rate is proportional to the current. The ion N_2O^+ appeared to be the active agent; the ions N_2^+, O_2^+, A^+ and He^+ were all without effect. The yield was estimated to be four molecules of nitrous oxide decomposed for each ion N_2O^+.

Zalogin and Egorova (36) produced oxides of nitrogen (determined as nitric acid) by high current discharge in mixtures of nitrogen and oxygen. Maximum yield was attained at 87–90% O_2, quite different from Laporte's maximum (35). Six milligrams of nitric acid were obtained per liter of gas mixture. The optimum mixture was independent of the current. Admission of ozone increased the yield of nitric acid.

According to Zenghelis and Evangelides (37) nitric oxide in silent discharge is partly (51.5%) decomposed into active nitrogen and oxygen, some of which forms ozone while part of the remainder is utilized in producing nitrogen dioxide. Part of the nitric oxide (25%) is oxidized to the peroxide NO_3 or N_2O_6, which combines with nitric oxide or the dioxide to form the pentoxide N_2O_5, a reaction which proceeds after cessation of discharge. The color changes as well as the formation of ammonia from water vapor proved the formation of active nitrogen.

Brewer and Kueck (38) studied the decomposition of nitrogen dioxide in glow discharge. The rate is proportional to the current in both the negative glow and positive column and is independent of the pressure. The reaction has a marked negative temperature coefficient. At 225° C. about 30 e.v. are required to decompose one molecule; at room temperature only 10 are required. The ions NO_2^+, N_2^+, O_2^+ and He^+ are almost equally effective in producing decomposition. The number of molecules decomposed per ion pair lies between 1.55 and 3, the lower value being more probable. The equilibrium at room temperature in the low-pressure arc is reached at 1.6% of nitrogen dioxide. A cluster type of mechanism accounts best for the results. A step process involving nitric oxide as intermediate would require a temperature coefficient of opposite sign from that found.

Briner and Wakker (39) discovered that the addition of small amounts of metallic lithium, calcium, barium and silver to the copper electrodes causes a large increase in the electrical arc fixation of nitrogen as nitric oxide or hydrogen cyanide. The gain is attributed to the low ionization potentials of these metals. The yields were 26.4 grams of HNO_3 and 12.3 grams of HCN per kilowatt-hour.

Later Briner and Wakker found that the following are favorable to the yield of nitric acid: increase of frequency of the alternating discharge, enriching air with oxygen and addition of lithium to the copper electrode. Yields as high as 88.4 grams of HNO_3 per kilowatt-hour were obtained at 1800 cycles, 50% of oxygen in air and 4% of lithium in the electrodes.

Stewardson (40) determined that, in the high-frequency glow discharge, with intense fields the rate of decomposition of nitrous oxide into its elements follows the first-order law better than any other in the pressure region around 1 mm. With weak fields the rate is independent of pressure.

Kobozev, Temkin and Fraiberg (41) studied the reactions of ozonized air containing 0.5% ozone on the oxides of nitrogen. The air was ozonized in a Berthelot ozonizer operating at 10,000 volts. A 10% mixture of nitric oxide in nitrogen was passed into the ozonized air, leaving an excess of ozone for the reaction

$$2NO + 3O_3 \rightarrow N_2O_5 + 3O_2$$

Reaction was instantaneous and 99% complete. If ozone is not in excess nitrogen dioxide as well as the pentoxide is formed. Introducing the mixture of nitric oxide and nitrogen into air and then passing through the ozonizer gave only nitrogen dioxide. But altering the ratio to $1NO{:}99N_2$, mixing with air and then passing through the ozonizer gave the pentoxide only. Ozone was found to have no effect on nitrous oxide.

Henry (42) observed the formation of oxides of nitrogen in Geissler discharge due either to excited atoms or molecules or to ions of atoms or molecules. The stoichiometric mixture $1N_2:2O_2$ gives the best yield. The reaction yield is much enhanced at liquid-air temperature. There is no reaction at room temperature and none in electrodeless discharge.

According to Balandin, Eidus and Zalogin (43) the formation of oxides of nitrogen in high-frequency discharge occurs by a chain mechanism. The primary products are ozone and nitrogen pentoxide. The latter yields nitrogen dioxide and oxygen. One kilogram of nitric acid is produced by 39.6 kw-hr. with an energy efficiency of 0.02%.

Brewer and Kueck (I, 17) measured the rate of synthesis of nitrogen dioxide in glow discharge. The rate is maximum at the beginning of the negative glow, from which it decreases exponentially with distance (Fig. 68). The yield per ion pair is estimated as 2 molecules of NO_2. The average path over which electrons ejected from the cathode are capable of initiating action is 0.36 cm. The number of positive ions per electron in the negative glow was 3.3.

Siegrist, Wakker and Briner (44) assert that increased yields of nitric oxide are attained at high frequencies in continuous discharge because of the lower temperature at which it may be operated. The addition of sodium, beryllium and ferrouranium to the copper electrode gave poorer yields, but calcium, barium, potassium and lithium increased them; 4.25% of lithium gave the greatest increase, 35%. An increase of as much as 60% was attained in semicommercial furnaces by using lithium-copper electrodes on oxygen-enriched air.

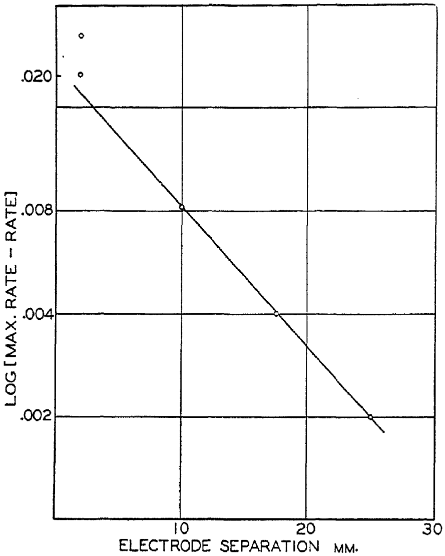

Fig. 68.—Rate of decay of reactivity through the negative glow. Synthesis of nitrogen dioxide. Pressure 0.3 mm. Hg; current = 5 milliamp. Brewer and Kueck, J. Phys. Chem. **36**, 2133 (1932).

(7.8.17) **Nitrogen-oxygen-chlorine compounds.** Hautefeuille and Chappuis (45), after having shown in 1881 (15) that the presence of chlorine inhibits the formation of ozone, found in 1884 that nitrogen, oxygen and chlorine unite in silent discharge to a crystalline solid $NClO_{13}$ which is volatile and decomposes at 105° C. without melting.

(7.15) **Nitrogen-phosphorus compounds.** Kohlschütter and Frumkin (IX, 74) demonstrated that nitrogen and phosphorus vapor combine in glow discharge to form solid compounds.

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CHAPTER XII

ACTIVE NITROGEN

The phenomenon of afterglow. When the current passing through a luminous gas at low pressure is interrupted it is found that in some cases the gas will phosphoresce or keep on emitting light even though the passage of electricity has been stopped. This phenomenon of afterglow was observed very early by E. Becquerel (1) in oxygen, and it appears that Geissler prepared his well-known "Geissler tubes" (2) in such a way that they showed an afterglow for several seconds. Morren (3) studied the phenomenon in mixtures of oxygen, nitrogen and sulphur dioxide and found that neither gas alone would show the effect but that all three gases were needed to produce the afterglow which was white in color and lasted for about 1 min. He thought that a compound $2SO_3 \cdot NO_3$ was formed in the discharge and that its decomposition and reformation were responsible for the afterglow. Sarazin (4) observed the same phenomenon in several gases and thought that oxygen was essential for its production and that chemical reaction was the cause of the phosphorescence. Goldstein (5) noted the effect in dry air but made no reference to its spectrum. Hertz (6) could not obtain the spectrum of the afterglow in nitrogen, but in air he observed a continuous spectrum especially strong in the red, yellow and green. The question arose whether the afterglow observed is produced in the body of the gas or on the glass wall of the vessel. Warburg (7) proved that the gas was the seat of the effect. He produced an afterglow in a discharge tube and opened it suddenly at one end, whereupon the luminosity was compressed into the other end and momentarily increased in brilliancy. He (8) showed further that a small amount of oxygen is needed to obtain the effect. Thomson (9) observed an afterglow in impure oxygen. It lasted for more than 1 min. under the electrodeless discharge with which he worked. Heating the bulb destroyed the luminosity and it did not appear in the hot gas. Cooling the gas made this afterglow appear again. Its spectrum was continuous. Air was the only other gas which showed the effect. The spectrum in this case was made up of bands or lines. Newall (10) studied the afterglow of oxygen mixed with nitrogen and carbon dioxide and noted, as Warburg had done, that the phosphorescent gas upon compression would flare up brightly. The spectrum he described as mainly continuous, with conspicuous bright bands in the region of the negative bands of oxygen. He also noted that no Tyndall beam is formed in the phosphorescent gas, and therefore solid particles (smoke) cannot be the cause of the phenomenon. It will appear later that he may have observed the afterglow of " active nitrogen." However, he ascribed it to oxygen, as his reference to the spectrum of the negative bands of oxygen indicates.

The afterglow of active nitrogen. It should be noted that the spectrum of the afterglow described so far appears mainly to have been continuous and no actual wave-length measurements had been made. Furthermore the conditions of excitation were those obtainable by the usual induction coil or the electrodeless discharge. The phenomenon of the "nitrogen afterglow" which bears this name at the present time seems to differ from these earlier observations, as was first pointed out by Lewis (11, 12). It is difficult to tell whether or not, for example, Sarazin, Morren or Goldberg observed this same afterglow that Lewis described, for these earlier investigators do not discuss their methods of excitation in enough detail. However, when it is realized that the conditions of excitation and the purity of the gas are of utmost importance in the production of the afterglow in nitrogen as pointed out by Lewis then one is inclined to the belief that there are several kinds of afterglow depending upon the condition of excitation and upon the state of purity of the nitrogen. The following discussion will deal with the nitrogen afterglow as produced by Lewis. He observed the ordinary known continuous afterglow in nitrogen with considerable traces of oxygen present, presumably when using an ordinary induction coil for the method of excitation. When chemically prepared nitrogen had been freed from the last traces of oxygen, no afterglow was observable with the ordinary induction current. However, he says that when a condenser and spark gap had been introduced into the secondary circuit: "a beautiful chamois-yellow mist filled the entire tube and pulsated several centimeters into the connecting tubes. On breaking the current a bright yellow afterglow lasted several seconds. At high pressures the thin white spark between the electrodes was surrounded by a sheath of this yellow pulsating cloud." Lewis measured the spectrum of this afterglow and found four bands with centers approximately at 6240, 5780, 5740 and 5410 Å. He identifies them with the nitrogen spectrum. When metallic sodium was introduced into the tube and used to remove even the last traces of water vapor and oxygen, the afterglow could no longer be obtained. Similar observations were made by Warburg (13), although Mosengeil (14) claims to have obtained the afterglow in nitrogen cleaned with sodium. It could not be obtained when using nitrogen prepared from air. The phenomenon depends upon the presence of very small traces of water vapor or oxygen. Lewis claimed that the yellow afterglow obtained by him differs from earlier observations in the following three respects: (1) it is produced only with condenser and spark gap; (2) it is seen only in nitrogen almost perfectly free from oxygen; (3) the spectrum is banded and not continuous.

Lewis (15) could produce this afterglow at pressures ranging from a few millimeters of mercury to as high as 35 cm. if the electrodes were placed correspondingly closer. He also noted, as had Warburg and Newall (7, 10) before him, that the phosphorescent cloud would be driven before the incoming gas mass whenever new gas was admitted to the experimental tube containing the afterglow. Small additions of hydrogen, carbon dioxide, water vapor and especially oxygen destroyed the afterglow instantly. Metallic lines of mercury and of the metal of the electrodes were also found in the spectrum of the afterglow. The luminescence of the mercury and aluminum showed a duration of at least 0.1 sec., but no afterglow of the metals appears unless there is also an afterglow of the gas.

Burke (16) studied the conditions of the afterglow produced by electrodeless discharge and found that the glow would travel from the place of production (the discharge) past wire gauzes placed in a long tube even though these gauzes were charged to high potentials. These experiments show that the phosphorescent gas does not emit light due to the presence of charged particles. The duration of the afterglow in air was studied by Trowbridge (17), as well as its spectrum, which was found to be similar to the bands observed by Lewis. It appeared then that the afterglow can be produced both by condensed and electrodeless discharge. Trowbridge observed the afterglow duration to vary from a fraction of a second to several minutes depending on conditions. For example, at liquid-air temperatures the glow died more rapidly than at higher temperatures, but it is brighter. The afterglow can also occur in a vessel at liquid-air temperature in which it was not produced. If the same vessel was used repeatedly the glow increased from 49 sec. to 14.5 min. in duration. Later on, the glow could be produced and lasted dimly for a period of 19 min. It appeared over a pressure range of 0.002 to 2.4 mm.

This yellow afterglow of nitrogen produced by condensed or electrodeless discharges was at first confused with a whitish afterglow obtained in air. However, gradually experimenters learned to differentiate and define the respective glows and state carefully the conditions of production.

Continuous and banded glow. A continuous afterglow in air was studied by Strutt (18), who did not obtain it in pure oxygen, while with air a bright yellow glow was observed which is improved by addition of oxygen. Pure nitrogen gives no glow whatsoever with an ordinary induction coil. Strutt ascribes the afterglow to the presence of ozone since (1) oxygen must be present; (2) it is destroyed by heat; (3) it cannot pass liquid-air temperature; (4) it is destroyed by passage over oxides of copper, manganese and silver; (5) the glowing gas oxidizes silver; (6) the gas beyond the glow does not do so. The glow appears to involve ozone and its consumption. Strutt looked for some other body which by using ozone may be responsible for the afterglow. He thought nitric oxide to be the other reaction partner. He, therefore, assumed the glow to be of purely chemical origin. However, it does not possess high temperature, nor does ozone made in an ozonizer and led into nitric oxide produce a glow, but NO gas prepared chemically and led into oxygen which had been through the discharge produces a yellow flash of light like the afterglow. Strutt also photographed the spectrum and found it continuous between 4200 and 6700 Å. The further statement is made that in these experiments drying the air seems to have had little influence. The glow from air is not appreciably effected by drying or by saturating it with water vapor.

Active nitrogen. However, Strutt (19) found later that a condensed discharge in pure nitrogen can produce the glow observed by Lewis which possesses a banded spectrum whereas the glow he had observed heretofore produced a continuous spectrum. Although Lewis was able to obtain his afterglow only from chemically prepared nitrogen, Strutt claims to have prepared it from nitrogen from air. The oxygen was removed from the air by red-hot copper. He also got the afterglow from atmospheric nitrogen which had been bubbled through molten phosphorus. The glow is not affected by the removal of ions. It is weakened by heating, intensified by cooling. This indicates it is due to the recombination of atoms. The modified nitrogen acts on ordinary yellow phosphorus forming the red variety; it combines with sodium and mercury producing in the latter case an explosive compound; it develops the line spectra of metals and the band spectra of compounds; it reacts with NO to form NO_2:

$$N + 2NO \rightarrow NO_2 + N_2$$

It attacks acetylene and the halogen derivatives of hydrocarbons, setting free the halogen and combining with the carbon to form cyanogen, as is shown by the brilliant cyanogen spectrum and by chemical tests.

These experiments of Strutt show that this new variety of nitrogen is chemically very active, and the suggestion that it is atomic nitrogen is of great interest. He makes the distinction as did Lewis that the glow of active nitrogen is different from the continuous afterglow in nitrogen obtained by the ordinary induction coil. This was shown in a spectroscopic study by Fowler and Strutt (20). They used various spectrographs and found that the spectrum of active nitrogen obtained with small dispersion is the same as that observed by Lewis (15). They describe the spectrum in three groups:

The first group comprises the conspicuous bands in the red, yellow and green with the brightest portions at 6252, 5804 and 5407 Å. Another faint band at 5054 is also part of this group. These bands belong to the first positive group of nitrogen.

The second group of afterglow bands extending from 4312 to 2503 Å form a connecting system of bands, although they have no evident relation to other known series of nitrogen bands. However, this group does not form a spectrum which exists exclusively in the afterglow. Its more intense bands were observed by Lewis in ordinary discharge through nitric oxide, and Fowler and Strutt observed them in air or nitrogen under suitable conditions.

The third group of bands from 3009 to 2155 Å degraded to the red belong to the third group of nitrogen bands as named by Deslandres. They are produced in the uncondensed spark in air, at atmospheric pressure in the arc between metallic poles, in the flame of cyanogen and in the flame of ammonia burning in air. Deslandres and Lewis incline to the view that they are due to an oxide of nitrogen, but Fowler and Strutt ascribe them to nitrogen. With all precautions to remove oxygen the bands have always been present in the afterglow spectrum even when the nitrogen had passed through molten phosphorus before it entered the discharge tube. The general behavior of these three sets of bands in relation to the afterglow is the same: They are produced in the ordinary uncondensed discharge, they disappear in the condensed discharge which produces the afterglow and they are present again in the afterglow spectrum itself.

In the condensed discharge which is needed to produce the afterglow a new series of bands of nitrogen was discovered by Fowler and Strutt. They called this new series the fourth positive group of nitrogen (2256–2904 Å). It does not appear in the afterglow spectrum. No afterglow is excited by a discharge which is so arranged as to give the atomic line spectrum only.

The new form of active nitrogen having been defined more precisely by its spectrum was next studied by Strutt (21) in respect to its chemical behavior. He found that oxygen destroys the afterglow although it does not combine with any of the species of molecules or atoms present in the discharge tube. He supposes that its action is catalytic, being analogous to that of cupric oxide. Hydrogen has no chemical effect; it only acts as a diluent to the luminous phenomena, without exhibiting its own spectrum. No ammonia was formed since the gases issuing from the discharge were neutral to litmus. Nitric oxide reacts with active nitrogen to form nitrogen peroxide (NO_2). The reaction gives rise to a greenish yellow flame with continuous spectrum. This flame is the same as is produced when nitric oxide is oxidized with ozone. At least, the continuous spectra of both reactions cover the same region of wave length. The same continuous spectrum is found in the mixtures (1) O_3 and NO; (2) O_3 and NO_2; (3) active N_2 and NO; (4) active N_2 and NO_2; (5) NO in a Bunsen flame and (6) NO_2 in a Bunsen flame. It is most probably due to the NO_2 molecule. Excess of NO added to active nitrogen gives a blue condensate (N_2O_3) collected at the exit end of a flow system. The percentage of active N_2 was determined, from the N_2O_3 formed, to be 2.5%. The active nitrogen reacts only slowly with the vapors of phosphorus and only after it has lost its luminosity! It appears then that active nitrogen does not lose its chemical reactivity at the same time that it loses its luminosity; in other words, a non-luminous modification of nitrogen seems to be indicated by this behavior toward phosphorus vapor. The afterglow had a rather large electrical conductivity comparable to the conductivity of flames although the afterglow is not dependent on the presence of ions. Liquid-air temperatures are not sufficient to cause condensation of active nitrogen. It appears that it is atomic in nature and that large molecular complexes are not present.

Spectrum production. The spectra of various substances can be excited by active nitrogen, as shown by Strutt and Fowler (22). The principal series of sodium appear with maximum intensity at 3303 Å. The spectra of iodine trichloride, mercury iodide are similar to the ones developed by these substances in a vacuum tube. The band spectrum of cuprous chloride is more completely developed in the afterglow than in the flame. Spectra of sulphur, hydrogen sulphide and carbon disulphide resemble the ones from a carbon disulphide flame in air. The cyanogen spectrum is developed in the afterglow by many organic substances with individual peculiarities. Strutt (23) found that active nitrogen emits its energy more quickly at lower temperature and on compression, showing that the process must be polymolecular. He distinguished the volume effect from the wall effect. For example, a bulb wet with concentrated sulphuric acid does not catalyze the decay of luminescence as readily as a glass bulb. He believed that Newall most probably observed the afterglow here discussed, since the band spectrum he ascribed to the negative glow of oxygen is remarkably close to the afterglow spectrum of nitrogen:

Oxygen negative glow 5985, 5870, 5592, 5248

Nitrogen afterglow 6252, 5804, 5407, 5054

The presence of oxygen. Although Strutt is inclined to ascribe the afterglow to nitrogen, which is certainly reasonable when it is remembered that its spectrum shows portions of the nitrogen bands only, others claimed that "pure" nitrogen does not exhibit the afterglow. It will be remembered that Lewis and Warburg had already failed to obtain the afterglow in nitrogen which had been treated with metallic sodium. Comte (24) did not think that phosphorus absorbed oxygen very rapidly and preferred to continue to treat the nitrogen gas with hot copper to remove the oxygen to such an extent that no afterglow resulted after passage of the usual condensed discharge. He concluded that oxygen is necessary for the production of the afterglow, since small additions of this gas would at once regenerate it. He did not, therefore, agree with Strutt, who ascribed the phenomenon to nitrogen only. But Strutt (25) thought that the phosphorus treatment could reduce the oxygen content to 1 part in 100,000 of nitrogen, and he still believed that the freer the nitrogen of oxygen the better the afterglow. Other impurities may of course prevent it. Lewis (26) pointed out the presence of the third positive group of nitrogen in the afterglow spectra, which are known to be due to nitric oxide (NO), whenever a little oxygen was present in the gas. However, the only invariable characteristic bands of the afterglow are the ones in the red, yellow and green regions belonging to the first positive group. He said that the intensity of the afterglow increased, in his experience, whenever the oxygen content decreased, and he believed that to date no one had worked with nitrogen free from oxygen or nitric oxide and obtained the afterglow. However, Koenig and Elöd (27) found that with improved purity of nitrogen, especially as concerns the removal of oxygen, the afterglow is stronger, and they sided with Strutt and ascribed the phenomenon to nitrogen only. It is quite evident that extreme purity of gas is needed to execute these experiments on active nitrogen afterglow, and one of the best methods of producing pure nitrogen is to prepare it from a metal azide. This method of preparation was used by Tiede and by Tiede and Domcke (28), who studied the afterglow in nitrogen made from barium azide or potassium azide and found that very pure nitrogen does not show the afterglow. However, addition of traces of oxygen from heated silver oxide immediately regenerated it. Naturally, they concluded that the afterglow somehow depended upon the interaction of oxygen, and they agreed with Comte and disagreed with Strutt, who ascribed the afterglow to nitrogen in the atomic state. They worked under very good vacuum conditions, avoiding stopcock grease, using liquid-air traps to remove mercury vapor and attempting to bake out their vessels and electrodes. Later (29) they found that they could remove traces of oxygen from nitrogen by means of heated copper to a sufficient extent to produce the afterglow and that for a given pressure of nitrogen a definite temperature of the Cu-CuO couple would produce the proper oxygen pressure for the afterglow to disappear. A definite higher temperature, on account of dissociation of the copper oxide, would cause the appearance of the afterglow just as it was at room temperature. When the system was in the condition where there was no afterglow, a small addition of oxygen from heated silver oxide would at once reproduce it. These experiments explain why Strutt could not obtain this afterglow from nitrogen passed over CuO at full red heat. They found that nitrogen (either from barium azide or free from oxygen by cupric oxide as outlined above) in the active condition and, therefore, containing some oxygen does react with iodine, sodium, sulphur, and thallium chloride, producing their spectra. However, oxygen-free nitrogen, free from afterglow, had no effect on the above substances.

Nitrogen atoms. Further evidence favoring the idea that active nitrogen consists of atoms is brought forth by Strutt (30), who showed that it is an endothermic substance and its energy of decay is of the order of the energy change of other chemical substances. He pointed out that the amount of ionization accompanying its decay is very small as compared with the number of neutral nitrogen atoms involved in the change. Only 1 nitrogen atom in 1500 concerned is ionized. Additional experiments were made to demonstrate that the disappearance of active nitrogen was more rapid at lower temperatures. He further (31) showed that active nitrogen (atoms) will have to make roughly 500 collisions on a copper oxide surface before they return to the normal state. The effect of impurities in the nitrogen used to produce the afterglow was recognized by Strutt (32), but he still believed that nitrogen alone is concerned. He found that 1 part of oxygen in 100,000 of nitrogen can definitely be detected by phosphorus fumes, and since he used phosphorus to remove oxygen from the experimental nitrogen, it cannot have contained more than 1 part of oxygen in 100,000 parts of nitrogen. Further treatment of the gas by copper oxide had no influence upon the phenomenon, and his experiments are in direct contradiction to the work of Comte (24). However, he noted that 2% of oxygen added destroyed the afterglow, 1% materially diminished the volume and the brilliancy and with 5% an entirely different phenomenon, the continuous ozone-nitric oxide glow, set in. The same facts are again stated later (33). These experiments showed that in order to get good results the nitrogen used should not contain more than 0.1% of oxygen. Other impurities were also studied. Both hydrogen and carbon dioxide (0.5 %) affect the glow. These gases are not so harmful as oxygen. Water vapor, however, is more injurious. Very dry nitrogen is required to get a good afterglow.

Chemical action. The chemical action of elements was further studied by Strutt. The explosive compound formed with mercury vapor and active nitrogen is a nitride, for it yields ammonia when treated with water. The metals zinc, cadmium and sodium give nitrides, as do arsenic and sulphur, shown in each case by subsequent formation of ammonia. Iodine did not yield a product which would furnish ammonia later. Carbon disulphide forms a deep indigo blue solid nitrogen sulphide $(NS)_x$ in the warmer portions of the experimental tube and a brown deposit in the colder traps. The brown deposit is a carbon monosulfide $(CS)_x$. The action may be written

$$CS_2 + N \rightarrow CS + NS$$

Sulphur chloride and hydrogen sulphide yield the ordinary sulphide of nitrogen, which gives ammonia when heated with potash. Stannic chloride yields a white deposit, of which Strutt did not obtain enough for identification. Titanium chloride shows the line spectrum of titanium, and a product able to give ammonia is formed. The organic compounds acetylene, benzene, pentane, methyl bromide, ethyl chloride, ethyl iodide, chloroform, bromoform, ethylene dichloride, ethylidenedichloride and ether gave hydrocyanic acid but not cyanogen. Carbon tetrachloride and carbon disulphide yielded no trace of hydrocyanic acid. However, compounds of the halogens behave differently. Chloroform and carbon tetrachloride produced a strong cyanate reaction, showing that they form cyanogen. Whether hydrocyanic acid or cyanogen was formed was tested by use of potassium hydroxide:

$$C_2N_2 + 2KOH \rightarrow KCN + KCNO + H_2O$$

In some of the cases cited the action is simple enough. With acetylene

$$C_2H_2 + 2N \rightarrow 2HCN$$

and with benzene

$$C_6H_6 \rightarrow 6CH;\ CH + N \rightarrow HCN$$

but other products are formed such as cyanobenzene C_6H_5CN and the isomeric phenylcarbylamine C_6H_5NC. As usual in electric discharge the products tend to be quite complicated, but Strutt pointed out that the method of active nitrogen activation may lead to some new organic syntheses. With pentane and similar hydrocarbons the excess of hydrogen above what is needed to make hydrocyanic acid is probably liberated in the free state or it may combine with active nitrogen to form ammonia. Neither possibility could be tested very well by Strutt. However, only a very small portion of the active nitrogen really reacted, less than 1%. The remaining 99% combined to the ordinary form without undergoing other chemical reaction. Most of the chemical actions cited are accompanied by luminosity (i.e., the cyanogen spectrum, for example) which, of course, is different in constitution from the spectrum of the afterglow, but it appears that these luminous effects are rather independent of the chemical ones, because there is no quantitative relation between luminosity and amount of chemical action.

New spectra. The use of active nitrogen as an agent for the production of new spectra would, of course, be of great interest to physicists, and several such spectra have been first obtained by this means. At this time Jevons (34) studied more carefully the spectra produced in silicon and titanium tetrachloride by the nitrogen afterglow. The new bands found with the silicon compound were not present in the silicon chloride spectrum itself and were, therefore, ascribed to a nitride of silicon. The titanium chloride, however, did not show any new spectrum which might be ascribed to a nitride. Similarly Jevons (35) found a boron nitride (BN) band spectrum when active nitrogen afterglow was allowed to act upon boron trifluoride or methylborate. These boron nitride bands also occurred in the electric arc spectrum of boron, but then they were mixed with boron oxide (BO) bands. But later Mulliken (36) claimed that they were due to BO even though excited by active nitrogen.

Ordinary discharge. Koenig and Elöd (37) produced active nitrogen in the direct-current luminous discharge in order to show that possible spurious effects accompanying the heavy condensed discharge ordinarily used should not be held accountable for the phenomena, The afterglow was readily induced by the luminous discharge at 15 mm., with an optimum pressure of 2–8 mm. They recognized the three characteristic bands (yellow, red and green), and they were able to repeat many of the chemical reactions which Strutt had studied. Nitrogen, hydrogen, water vapor and, surprisingly, oxygen showed no reaction but acted only as diluents. Of the hydrocarbons, methane is most active towards active nitrogen; others gave hydrocyanic acid and the cyanogen bands. HCN could be found only in traces, but ammonia was formed as well as amylene. They further proved that both nitrogen and oxygen must be activated in the discharge in order to react to form oxides of nitrogen. They (38) produced the afterglow in nitrogen which had been heated in a potassium vapor discharge until the third group of nitrogen bands (due to NO) had disappeared. The potassium vapor was removed by cooling. In other words, they obtained results in agreement with Strutt and in opposition to the work of Tiede and Domcke, whose results they explained by the presence of mercury vapor which extinguished the afterglow. But Tiede and Domcke (39) claimed that their gases were free of metal vapors. Another investigator, de Kowalski (40), became interested in the afterglow and produced it by electrodeless discharge with nitrogen which had been purified from oxygen by means of potassium.

Is oxygen necessary? This question has still not been settled to the satisfaction of several interested parties, and it is seen that one faction of investigators (Lewis, Comte, Tiede and Domcke) insisted that oxygen was needed to produce active nitrogen. However, Baker, Strutt, Koenig and Elöd maintained that the afterglow can be produced in the purest nitrogen and that phosphorus was a proper means of removing oxygen from the nitrogen (to 1:100,000). Naturally, the controversy continued, and Baker and Strutt (41) repeated the experiments of Tiede and Domcke (39). They prepared their nitrogen from fused potassium azide; they heated the glass wall of the apparatus and the platinum electrodes even to red heat to drive out occluded gases. And they always obtained the afterglow in an apparatus which contained the metallic potassium from the decomposition of the azide, so that very little oxygen could have been contained in the gas phase! In another experiment employing liquid sodium-potassium alloy and, of course, nitrogen, the afterglow was obtained even after 21 days! The liquid alloy maintained its luster throughout the whole time. Naturally, they contended that oxygen was absent and that the afterglow is due to nitrogen and nitrogen only without the intervention of any oxygen. Nor could they obtain the results of Tiede and Domcke with copper oxide. They always found the afterglow. But they said, even granting their opponents' contention, i.e., that oxygen is needed for the appearance of the afterglow, that does not disprove their argument that active nitrogen exists, as can be readily seen when the remarkable chemical actions are recalled which this active nitrogen can produce in a great variety of substances. And surely ordinary nitrogen even containing traces of oxygen could not possibly be so reactive.

The situation was certainly baffling. Both groups of experimenters worked with greatest care and obtained different results. Tiede and Domcke could produce nitrogen which would not show the afterglow. They could regenerate it by adding a little oxygen. Baker and Strutt could get the afterglow even in purest nitrogen prepared in the same way as used by their opponents. In view of this remarkable contradiction it was agreed that Tiede and Domcke should go to London to perform their experiments in Strutt's laboratory. The results (42) of these combined efforts were the following: In Tiede and Domcke's discharge tube and with their electrical equipment the afterglow did indeed diminish greatly in brilliancy and could be restored by addition of very small amounts of oxygen. On the other hand, when Baker and Strutt's tubes were used it was not found possible to reduce the afterglow even in nitrogen prepared by Tiede and Domcke. It appeared that the form of discharge tube used by the English investigators was more favorable to the production of the glow and that a trace of oxygen may condition the discharge in a manner more favorable for afterglow production. This situation was rather unsatisfactory, and the question was studied further by Strutt (43), who pointed out the difference in the shape of the discharge tubes used by the German and English investigators. The former used a rather narrow tube (Fig. 69A); Strutt and co-workers used a vessel containing a large bulb (Fig. 69B).

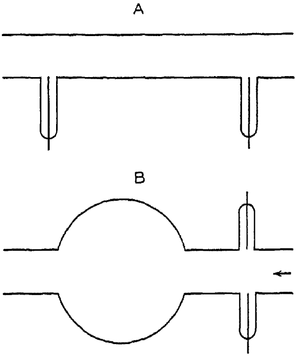


FIG. 69.—Discharge tubes for the production and study of active nitrogen. A. Tube used by the German investigators. B. Tube used by the English investigators. Strutt, Proc. Roy. Soc. 91, 303 (1915).

Traces of other gases. Strutt, continuing the investigation, found that he could produce nitrogen by treatment with sodium-potassium alloy at 300° C. so free from oxygen that the glow was greatly reduced but not entirely extinguished. Furthermore, he noticed that admission of oxygen at the rate of 3.5 cc. (NTP) per hour brought the afterglow to its maximum effect. More or less oxygen was not so satisfactory. Two per cent oxygen killed the afterglow. This optimum amount represented a concentration 1:750 relative to nitrogen. Yet he had removed oxygen from nitrogen by means of phosphorus to a relative concentration of 1:100,000 and produced the glow! He, therefore, concluded, "Minute admixtures of gases other than oxygen are capable of performing the same function and can act as catalysts for promoting the formation of active nitrogen in the discharge." Methane strongly restored the glow but was used up by the active nitrogen, so that the glow became very dim when admission of methane was stopped. Ethylene, acetylene, carbon monoxide, carbon dioxide and sulphur dioxide behaved similarly. Hydrogen sulphide produced an especially bright glow, and when its flow was stopped the glow continued. In order to return the tube to its former condition of dim glow, it had to be washed with aqua regia to remove sulphur from the walls of the apparatus! Chlorine restored the glow faintly; hydrogen had only a very feeble effect; the rare gases helium and argon had no effect whatever. Mercury vapor brought forth the glow as does water vapor. From the variety of gases employed it appeared that almost any foreign gas could restore the glow, and oxygen was certainly not the only gas which acted upon the nitrogen and its oxidation surely was not necessary in order to produce the active nitrogen or the afterglow. To explain the discordant results obtained by the various investigators it may be supposed that accidental impurities controlled their experiments. As to the action of these catalysts and their ability to destroy active nitrogen, Strutt believed that their electron affinity had some bearing on the problem. He did not mention the possibility of wall reaction or catalysis, which later view, it will be seen, is the modern explanation of this remarkable phenomenon.

Further studies. A few additional chemical studies were made by Strutt at this time. He found that active nitrogen did not affect a clean quiet surface of mercury, but that drops of mercury, kept in motion, form the nitride and extinguish all the glow but do not emit the mercury spectrum as was the case when the vapors of mercury reacted with the activated nitrogen. Bismuth-tin alloy, molten tin and lead behaved in a similar manner. The glowing gas could be bubbled through glycerin without any ill effects, but a solution of indigo in concentrated sulphuric acid was decolorized.

Active nitrogen reacted with many compounds to form hydrocyanic acid. In the case of the paraffins, however, Koenig and Elöd

(38) found none with pentane. But Strutt obtained it with heptane, pentane, and methane. The condensed discharge used for the production of active nitrogen was replaced by Strutt (44) in his next experiments by the luminous direct-current discharge, and he showed that its production was greatest near the cathode, fell to a minimum in the Faraday dark space and became larger in the positive column without, however, reaching the values near the cathode. More active nitrogen was obtained from the positive column in a narrow than in a wide tube, the current being constant. Since the potential gradient was about the same in both size tubes the controlling factor must be the current density, which also explained the action of the condensed discharge where high currents flowed for short periods. But the discharge not only produced but it also destroyed the active nitrogen, for only a maximum concentration could build up for given discharge conditions. A trace of oxygen greatly increased the afterglow and it also lowered the cathode drop; however, the potential drop in the positive column was not affected. Active nitrogen was also produced in sparks at atmospheric pressure but could not usually be observed because of the destructive effects of the gases surrounding the spark. The metal sputtered from the cathode of a discharge tube showed its line spectrum in active nitrogen.

The situation regarding active nitrogen was reviewed by Koenig (45), who stated that the conditions for the production of the afterglow of sufficient intensity for visual detection are: (1) The gas must have the greatest purity. (2) The product of gas pressure and diameter of discharge vessel must not have too small a value (at pressure of 1 mm. Hg and less, the afterglow can be observed only in wide tubes or in bulbs). (3) The activating discharge must have sufficient intensity. For example, de Kowalsky (40) could produce an afterglow in a sample of nitrogen by using a more powerful discharge when a weaker current had no effect. The second condition is very important for the proper production of the afterglow.

The earlier spectroscopic study of the afterglow by Strutt and Fowler (22) was continued by Strutt (46), who paid particular attention to observe it, well shielded from the original discharge, so as not to contaminate the spectrum of the afterglow with any lines or bands produced in the discharge proper. He further studied the effect of small amounts of impurities on the spectrum of the afterglow. He established the following facts:

(1) The faint red bands 6394.45, 6468.53, 6544.81 and 6623.52 Å which belong to the first positive group are also part of the spectrum of the afterglow of active nitrogen.

(2) The second positive group of nitrogen does not belong to the aftergow.

(3) The β and γ groups appear only when oxygen-containing gases are added to the afterglow, but no definite conclusion is reached as to their origin.

Later Strutt (47) found that addition of helium, neon or argon would shift the intensities in the first group bands toward the red.

Triatomic nitrogen. It must appear that, so far, the results of experiments point to the conclusion maintained by Strutt that active nitrogen consists of atoms and that the afterglow is due to nitrogen molecules. Others had different ideas, and one suggestion made at this time by Trautz (48) was that, in analogy with ozone, active nitrogen was a triatomic form of nitrogen:

$$N_2 \rightarrow 2N \text{ (in the discharge); } N_2 + N \rightarrow N_3 \text{ (active form);}$$

$$N_3 + N \rightarrow 2N_2 \text{ (decomposition and glow)}$$

Since, however, this suggestion does not explain later facts, it is not of interest to discuss the detailed calculation made by Trautz at that time.

Decay of luminosity. An interesting advance in the study of the afterglow was made by Angerer (49), who showed that the law of decay was not exponential but that the square root of the intensity of the afterglow was proportional to the time of decay. This indicated the order of the decay reaction, whatever its detailed nature, to be bimolecular. Angerer used an electrodeless discharge made by Zenneck (50). Once more the argument regarding the carrier of the afterglow was taken up by new investigators. Pirani and Lax (51) studied the discharge of a 100,000-cycles-per-second current in a large vessel (2.1 liters) in nitrogen, and they claimed that pure nitrogen did not show the afterglow, but the presence of electronegative gases (O_2, H_2O, I_2) is needed to obtain it. Rare gases and electropositive ones (H_2) had little effect.

Phosphoresence of solids. From the potent nature of active nitrogen one would suppose that it could initiate all sorts of effects which demand application of energy in some form. It is easily understandable then that Lewis (52) found that he could induce phosphorescence by active nitrogen impinging on a variety of substances. The phosphorescence induced was of continuous spectral character except in the first two substances mentioned:

Strong phosphorescence. Uranium nitrate, uranium ammonium fluoride, zinc sulphide, barium chloride, strontium chloride, calcium chloride, cesium chloride (order of brightness).

Weak. Lithium chloride, sodium chloride, potassium chloride, sodium iodide, potassium iodide, sodium carbonate, strontium bromide.

No effect. Potassium sulphate, potassium nitrate, potassium hydroxide, mercurous bromide, calcium carbonate, calcium sulphate, calcium sulphide, lead chloride, cadmium iodide, magnesium nitrate, zinc chloride, manganese chloride, thorium oxide, chalk, sugar, quinine sulphate.

To this list Jevons (53) added aluminum chloride. Krepelka (54) noted a bright green phosphorescence lasting 1 min. in a tube containing aluminum chloride and aluminum, cooled by a stream of nitrogen. Tiede and Schleede (55) made observations similar to those of Lewis on lithium fluoride, lithium carbonate, beryllium carbonate, beryllium oxide, boron nitride, barium platinocyanide, magnesium carbonate, calcium azide, barium azide, molybdic acid, terphthalic acid and isophthalic acid.

Quantum theory. Metastable molecules. One of the first attempts to explain the behavior of nitrogen in the active state in terms of modern quantum concepts was made by Saha and Sur (56), who believed that active nitrogen consisted of excited molecules having about 9 e.v. of energy. The afterglow band in the visible cannot be related to the ground state of nitrogen molecule because ordinary normal molecular nitrogen is transparent in the visible. It has, however, an absorption spectrum in the region 1200–1600 Å (or 10–8 e. v.), and the lower state of the visible afterglow bands is then an excited state of nitrogen about 8.2 e. v. above normal. Foreign substances will prevent the return of the excited molecule with light emission, producing, according to Klein and Rosseland (57) and later Franck (58), radiationless transfers. Saha and Sur could in this way at least indicate a reason why, for example, certain mercury lines can be excited and why others do not appear. The reason is that the excited nitrogen molecules (active nitrogen) have available only about 8.2 e. v. of energy and that the term values of some of the mercury lines lie higher than this amount. It also explains why hydrogen and the rare gases have no influence on the afterglow. Their lowest energy levels are of greater amount than 8.2 e. v.

Birge (59) then attempted to give a more detailed picture of the constitution of active nitrogen. He based his deduction on the results of the spectroscopic investigation of nitrogen. The afterglow bands are part of the first positive group of nitrogen, and the strongest of each of the four groups forming the so-called alpha bands correspond (in emission) to a transition from vibration level " 11 ". This level and the nearest one with vibrational numbers 10 and 12 are almost the only ones involved in bands of the afterglow. He supposed, therefore, that this initial state is metastable for 10, 11, or 12 units of vibrational energy. Rotational energy does not seem to be important in determining the initial or for that matter the final state of the nitrogen molecule when it gives out the afterglow. Saha and Sur (56) did not consider the initial state metastable as Birge did. Birge thought this point one of importance. He believed that the initial state must be a metastable one because, while active nitrogen was formed in the discharge, it was able to diffuse into the side arms of the apparatus where it gradually changed back into ordinary nitrogen with emission of the alpha bands. While then the vibrational state of the nitrogen molecule is the eleventh level, it is not known where this state is located in relation to the normal. Birge made a guess that its energy is about 11.5 e. v., whereas Saha and Sur assumed it to be an excited molecule of 8.5 e. v. energy.

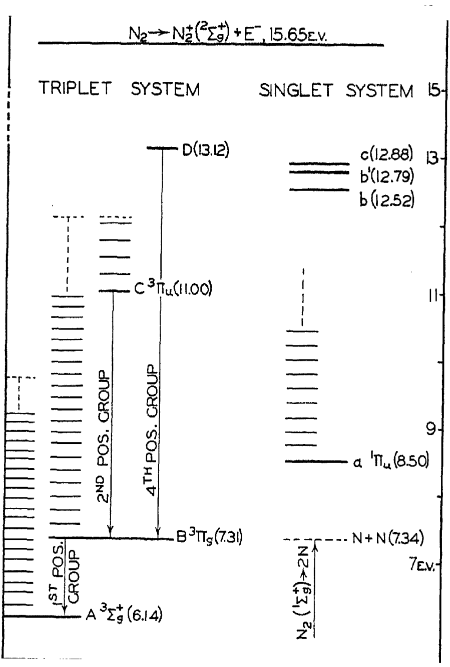
The fact that a small amount of electronegative gas is beneficial for the production of the afterglow Birge explained on his theory by the assumption that electron collisions were effective in causing the reversion to normal of metastable molecules and that the electronegative gas (oxygen) caught the electrons and made them inoperative in regard to their behavior towards metastable molecules.

The conclusion that nitrogen must consist of metastable molecules was also reached by Foote and Ruark (60). They produced the afterglow of active nitrogen in electrodeless discharge and found this mode of activation very effective. They obtained mercury lines by active nitrogen requiring 9.5 e. v. for their excitation. Later Foote, Ruark and Chenault (61) found that the mercury lines requiring 9.52 e. v. for their production were strongly developed whereas even exposures to 150 hours did not bring out mercury lines needing 9.66 e. v.

Further production of spectra. Just as Strutt and Fowler (22) and Jevons (34, 35) had produced band spectra, so Mulliken (62) obtained the bands of CuF, CuCl, CuBr and CuI. Certain bands due to CuO must have come from an oxygen impurity. Results similar to the above were obtained with PbI_2, HgI_2 and $HgBr_2$. The mechanism of production of these spectra is the one proposed by Saha and Sur (56), namely, excited nitrogen molecules, by " impacts of the second kind," put the halide molecules into high excited states necessary for the emission of these band spectra. However, a fair number of such impacts also result in dissociation as the iodine arc line 2062 Å and more than eighty copper arc lines have been identified. Mulliken was able to study the isotope effect of Cu (63) and Cu (65) in these band spectra. He thought that Birge's estimate of 11.4 e. v. for the excited state of the nitrogen molecule is too high and should be reduced to 10.4 e. v. The true energy must be somewhat higher since the active nitrogen was in a metastable state, according to Birge, which presumably differed from the emitting state. The band spectrum of gold chloride was similarly obtained by Ferguson (63), but the attempt to excite gold bromide and iodide failed.

A very long-lived afterglow was obtained by Rudy (64) lasting in some cases 15 min. He found the law of afterglow decay to be bimolecular, though he did not give detailed information. The temperature coefficient was much smaller than for ordinary chemical reactions in the range 20–130° C. A magnetic field had no effect on the decay of the afterglow. He noticed particularly the complete absence of nitrogen atomic lines from the afterglow spectrum. A tube containing nitrogen and helium at several centimeters' pressure showed an orange afterglow, as was usually the case at high pressure, and all the strong nitrogen lines were present in the discharge. The same gases at lower pressure gave a strong afterglow, but only helium and nitrogen molecular spectra were then obtained in the discharge. The afterglow was, of course, obtained in nitrogen alone, and then no atomic lines were found even though another discharge was sent through the afterglow itself. Worthing and Rudy (65) obtained two afterglows in nitrogen (0.2%) and argon (98.8%) mixtures. With tungsten electrodes an orange or blue afterglow was obtained. The orange glow was of the usual type; the blue glow, obtained at high temperature and more severe discharge conditions, also showed some tungsten lines, and tungsten nitride appeared to be formed. With nickel electrodes, the second type of glow contained the lines of atomic nickel. It is then possible to excite some of the line spectra of the heavy metals by means of active nitrogen. No argon lines were found either in the discharge or in the afterglow. The afterglow itself was stronger in the argon-nitrogen mixtures than in pure nitrogen itself. An unusual intensity distribution of the first positive group of nitrogen was found by Johnson (66). In a general way it resembled the distribution in the afterglow.

Energy levels of nitrogen. A most interesting contribution to the study of active nitrogen was made by Miss Sponer (67) when she determined the minimum electron velocity necessary to excite certain band spectra of nitrogen. She used the method of electron impact and found for example that the well-known zero vibration band (3371 Å) of the second positive group of nitrogen is excited by 13.0 e. v. Therefore the excitation potential of the zero band of the first positive group is 9.3 e.v. Rudberg (130) and Brindley (144) have measured the energy losses of electrons in nitrogen. The latter's values check better with the known term system. He finds losses at 8.6, 12.2 and 12.9 e. v. referring to the singlet levels *a*, *b*, *b′* and *c* of Fig. 70. These values fit reasonably well into the scheme adopted for the term system of the nitrogen molecule. Mulliken (91) suggested that the heat of dissociation of nitrogen (148) be taken to be 9.0 e. v., with 7.8 e. v., for the non-vibrating $A^3\Sigma_u^+$ state (see also page 288).



$N_2 \rightarrow N_2^+(^2\Sigma_g^+) + E^-$, 15.65E.V.
TRIPLET SYSTEM
SINGLET SYSTEM
15
D(13.12)
c(12.88)
13
b′(12.79)
b(12.52)
$C\,^3\Pi_u$(11.00)
11
2ND POS. GROUP
4TH POS. GROUP
9
a $^1\Pi_u$(8.50)
$B\,^3\Pi_g$(7.31)
N+N(7.34)
7E.V.
1ST POS. GROUP
$A\,^3\Sigma_g^+$(6.14)
$N_2(^1\Sigma_g^+) \rightarrow 2N$

FIG. 70.—Energy level diagram of the nitrogen molecule. Herzberg and Sponer, Z. physik. Chem. B26, 1 (1934).

Miss Sponer revived the hypothesis, advanced earlier by Strutt, that active nitrogen is atomic nitrogen. This view seemed more plausible at this time because atomic hydrogen had been studied in the meantime by several investigators after Wood (68) had shown how to produce it in discharge tubes. Bonhoeffer (69) had shown that impurities such as oxygen and water vapor decatalyzed the walls which then could serve no longer for the recombination of hydrogen atoms. Metals serving as catalysts for recombination became white hot in a stream of atomic hydrogen. From the long life it appeared that atomic hydrogen could not recombine in the gas phase by double collision but that triple impacts were necessary for successful recombination. Furthermore, impacts of the second kind were possible, and the D-lines could be excited when atomic hydrogen had a chance to act on sodium. Miss Sponer then proposed by analogy to apply these ideas to active nitrogen. The difference lies mainly in the greater heat of dissociation, which is even sufficient to raise a normal nitrogen molecule in a triple collision to an excited state. From these considerations it appeared that the heat of dissociation of nitrogen should be about equal to the excitation energy of the eleventh vibrational level of the nitrogen molecule in the initial state from which the first positive bands originate. This gave for this quantity 11.4 e. v. Any impurity or admixture of gas which can be brought to luminescence can show only such radiation as originates from a term whose value is less than 11.4 e. v. The small admixture of oxygen which caused so much trouble in earlier studies is needed to decatalyze the wall as in the behavior of Wood's hydrogen. In order to produce active nitrogen, then, it is necessary to have a discharge so powerful that plenty of nitrogen molecules are produced which have more energy than the heat of dissociation. As a matter of fact, Strutt did find that the production of active nitrogen is especially good when the fourth positive group of nitrogen appears in the discharge. Its excitation potential is about 14.8 e. v. Birge realized that there were objections to the metastable state which he proposed for active nitrogen, and he (70) agreed with Sponer that active nitrogen must be atomic in nature.

Conflicting views. But not all investigators accepted as yet the atomic hypothesis. Willey and Rideal (71) believed that active nitrogen consisted of metastable molecules of about 42,000 cal. activation energy. This quantity they determined from calorimetric experiments on the supposition that one active nitrogen molecule can oxidize only one nitric oxide molecule in its active life. This value would then be a lower limit of the energy content of active nitrogen. But such a small value for the energy is not easy to understand, when it is remembered that Strutt could excite the iodine line 2061 Å which needs at least 150,000 cal. for its excitation, as pointed out by Ludlam and Easson (72). Active nitrogen molecules of 43,000 cal. energy would have to make several successive impacts with a given iodine molecule in order to raise its energy the required amount or several active nitrogen molecules would have to make a collision simultaneously. But either process seems very unlikely when it is considered that iodine vapor extinguishes the afterglow in a fraction of a second and this rapidity indicates that the energy exchange takes place in one impact between one activated nitrogen molecule or atoms and one iodine molecule. By implication the energy content of active nitrogen must be equal to or greater than 150,000 cal. Johnson (73) came to a similar conclusion; he remarked that active nitrogen of 2 e. v. energy cannot possibly account for the various spectra excited by the afterglow including its own, for the molecules after emission of the alpha bands (first group) are in an energy state of 8 e. v.

Electrical properties. Once more several investigators became interested in the electrical properties of active nitrogen, and Kichlu (74) and Constantinides (75) confirmed Strutt in the observation that no free ions existed in active nitrogen. However, Constantinides found that free electrons can be removed from electrode metals either by photoelectrical or direct impact action of active nitrogen. He also studied the action on the duration of the afterglow of the gases helium, nitrogen, oxygen and hydrogen. Of special interest is the fact that helium had no effect on the afterglow, showing that no energy could be transferred to this atom because its lowest excitation potential, 19.7 e.v., is already higher than the energy of active nitrogen which is of the order of 10.0 e.v. if the atomic theory is accepted. Constantinides further found that active nitrogen did not ionize hydrogen or mercury vapor but that ions were formed in iodine gas. He therefore stated that active nitrogen consisted of metastable molecules having 9.4–10.4 e.v. of energy. Rayleigh (76) pointed out that the facts established by Constantinides were scarcely sufficient to warrant the view that active nitrogen is not atomic but consists of metastable molecules.

The effect of the wall. However, Bonhoeffer and Kaminsky (77) adopted Strutt and Sponer's atomic view. They again showed that pure nitrogen did not glow alone but that $1^0/_{00}$ of foreign gas was needed. But as this added gas had no influence upon the spectrum of the afterglow it could not be of importance in the production of luminosity directly, but was of great moment in determining the character of the wall. By decatalyzing the glass surface the added gases helped in the production of the afterglow. Bonhoeffer and Kaminsky also showed that the decay of luminosity was a bimolecular reaction, but they were not able to show that triple collisions were needed. In the ultraviolet and in the visible region of the spectrum the glowing active nitrogen showed no adsorption of light. They found the spectrum of the exciting discharge in very pure nitrogen, and hence free of an afterglow, to be the same when small amounts of impurities were added and thereby an afterglow was produced. In this respect active nitrogen behaves differently from active hydrogen. Lewis (78) suggested that two-body collisions may be possible between nitrogen atoms leading to combination since the molecule so formed possesses quantum states of appropriate energy from which it could radiate. This idea would make the assumption of triple collisions unnecessary and might explain Bonhoeffer and Kaminsky's results.

Further research. The situation regarding active nitrogen was reviewed by Ruark, Foote, Rudnick, and Chenault (79); they studied the afterglow and the production of metallic spectra. They found second positive group bands besides the bands of the first positive group of nitrogen when a little mercury vapor was present, but it is known now that in pure nitrogen only the alpha bands are part of the afterglow spectrum. Mercury atoms can receive at least 10 volts of energy from active nitrogen. Mercury azide decomposition cannot be involved in the metal excitation on thermochemical grounds. The bulk of the evidence seemed to point towards the atomic constitution of active nitrogen. Okubo and Hamada (80) carried out a similar investigation on active nitrogen but they could not obtain the beta band even after 60 hours' exposure. They found arc lines of many metals but no spark lines although the ionization potentials of some of them were less than the energy which active nitrogen can transfer. They were able to obtain spectral lines (after 4 hours' exposure) in mercury whose potential is 9.56 e.v., but 100 hours of exposure would not show lines whose excitation potential is only 0.14 e.v. higher. Ruark (79) claimed that the difference in results in the last two researches mentioned might be due to the difference in pressure used by the two groups of investigators.

That transfer of energy depends on the specific nature of the atoms and molecules involved was held by McLennan, Rudy and Anderson (81), for xenon cannot be put into a metastable state which is known to exist at 8.4 e.v. Since addition of mercury to the xenon-nitrogen mixture brought out the mercury lines they supposed that the emission of light was a matter of chemiluminescence. Findlay (82) also presented this idea. No calcium lines were found in the afterglow, probably on account of stable nitride formation, but sodium and potassium lines appeared. Again with indium no lines were observed, and Findley supposed that it forms no nitride. Nothing was said regarding the vapor pressure of these metals. Then again the auroral green line 5577.35 Å was obtained in a mixture of nitrogen and 4% oxygen, as was shown by Kaplan (83). Easson and Armour (84) found iodine lines of 8.4 e.v. excitation potential. Band spectra could be produced by active nitrogen, as has been mentioned before, and Knauss (85) obtained carbon monoxide bands of excitation energy 8.2 and 9.0 e.v. while hydrogen was not affected.

Willey and Rideal (86) continued their studies of the chemical effect of active nitrogen; they still believed that the chemical evidence pointed to an unstable molecular form of about 2 e.v. energy content. Studying several chemical activations, they found that hydrogen, oxygen, water, carbon dioxide, carbon monoxide, chlorine, bromine, iodine, methane, hydrogen chloride and nitrous oxide were not affected chemically but that ammonia, hydrogen bromide, hydrogen iodide and nitric oxide were decomposed into their elements and that hydrogen chloride synthesis was possible. The above substances formed two classes of high and low activation or decomposition energy. The limit seemed to be about 55,000 cal., and Willey and Rideal concluded that active nitrogen was able to transfer most readily about 45,000 cal. to a reacting system, causing it to change, and that therefore its energy content was of the same order. Willey (87) deduced the same value from a study of the catalytic activity of metals in active nitrogen. In order to reconcile his views and the atomic theory of active nitrogen he proposed to show that active nitrogen really consists of two species of varying energy. The atoms are responsible for the luminous phenomena of the afterglow which is produced by impacts of the second kind as are all other spectra observed in the afterglow. The chemical activity, however, is due to another modification of lesser energy content (45,000 cal.). Willey (88) therefore showed that luminosity and chemical activity are not concomitant. He destroyed the afterglow of active nitrogen by an auxiliary discharge and determined the concentration of active nitrogen by means of thermometers further downstream, finding that for weak auxiliary discharges the concentration of active nitrogen was the same with or without them. He determined the concentration of chemically active nitrogen by reaction with nitric oxide and found it independent of the glow. Furthermore, chemically active nitrogen was produced in a high-tension arc at high pressure where the usual luminous phenomena of active nitrogen were absent. However, no guarantee exists that the usual species of active nitrogen is present in the arc. Willey then destroyed the afterglow by heat and still found the usual chemical activity downstream towards nitric oxide of the active nitrogen so treated. Again it appears that luminosity and chemical activity are indeed independent phenomena.

Strutt and also Willey had shown that active nitrogen and molecular hydrogen do not react, and several investigators (89) obtained conflicting results when they attempted to form ammonia from atomic hydrogen and molecular nitrogen. However, Lewis (90) obtained ammonia formation when active nitrogen and atomic hydrogen, separately produced, were allowed to mix. No hydrazine was formed. Activation of either gas alone gave no ammonia. From the fact that both gases had to be activated Lewis believed that atomic nitrogen was present in active nitrogen. He cited as favorable to his view the fact that Caress and Rideal (V, 23) obtained ammonia formation at

13 volts, which would indicate that they had to produce atoms before they obtained any ammonia. However, the voltage measurements in such "slow electron activation" experiments are not wholly certain as yet, and the energy diagram of the nitrogen molecule is not completely worked out, as Mulliken (91) pointed out. That both gases must be activated to obtain ammonia is of interest. Willey (92) claimed that ammonia can be formed from active hydrogen and ordinary nitrogen and that activated nitrogen acting on ordinary hydrogen gave no ammonia, for the reason that ammonia is known to be decomposed by active nitrogen with destruction of the glow. But Lewis (93) points out that the ammonia was collected very rapidly and so some of it escaped the destructive action by active nitrogen. He also cited numerous examples of action by active nitrogen which showed, as does the production of spectra, that it carried more than 2 e. v. of energy.

Kaplan (94) now entered the field, and in his first experiments he recorded the beta bands of nitrogen as belonging to the afterglow. He then agreed with Ruark et al. (79) but differed with Okubo and Hamada (80) and Kichlu and Basu (95). He pointed out that the excitation potential of the zero-zero bands of the second group (beta) band was 13.0 e.v. and that this value was greater than the heat of dissociation of nitrogen which was at the time 11.8 e. v., so that the atomic mechanism of Strutt and Sponer would be in difficulty.

Following Bonhoeffer and Kaminsky who studied the possible catalytic effect of traces of gases, Herzberg (96) found that thoroughly baked-out vessels do not permit the afterglow to form, even in mixtures of nitrogen and oxygen, by electrodeless discharge. Similar experiments were reported by Majewska and Bernhardt (97), Majewska (98) and Stöck (99). Herzberg found that a clean quartz surface was a good catalyzer for the non-luminous atom recombination. The earlier findings that a trace of oxygen in pure non-glowing nitrogen will restore the glow must be interpreted now to mean that the added oxygen modified the conditions of the wall by poisoning it for the catalytic recombination. Indepdendent experiments were carried out by Lewis (100), who also found a reversed temperature and pressure effect. With untreated vessels duration and intensity of the afterglow increased, as pressure and temperature decreased; the reverse was true with clean vessels. Paraffin surfaces did not act as catalysts for the recombination of atoms. The further remarkable fact was discovered by Herzberg that small traces of hydrogen and oxygen produced a great increase in the intensity of the afterglow. These traces of hydrogen seemed most effective in decatalyzing the walls. Larger amounts had no particular effect on the afterglow. But, when a discharge was sent through pure hydrogen, the hydrogen removed and nitrogen substituted, no afterglow was produced, so that mere absorption of the hydrogen was not sufficient to poison the wall. It appeared that some compound between hydrogen and nitrogen produced the poisoning effect on the walls of the vessel. Glass vessels behaved somewhat similarly to quartz tubes. An afterglow due to oxygen was also observed, and under certain conditions the walls of the vessel showed phosphorescence.

As earlier investigators had already shown, so again Koenig and Klinkmann (101) found that the integral luminosity decayed bimolecularly and the decay time of the individual bands of the alpha group decreased from the red to the violet and the alpha group had a greater decay time than the beta group, indicating the presence of several processes. Willey (102) also came to the conclusion that the decay was of the third order. Kneser (103) took into consideration the deactivation on the walls and found for the gas phase reaction, with varying amounts of argon present, that his results agreed with the assumption that decay took place between two active atoms and one non-active particle. The same author (103) summarized the work on active nitrogen in an excellent article.

Willey (104) produced iron nitride in an arc of nitrogen between iron electrodes in which the afterglow could not be detected. This observation points toward a non-luminous active nitrogen modification.

The spectroscopic knowledge of the afterglow was extended by Kichlu and Acharya (105) when they found some of the infra-red bands of the first positive group of nitrogen in the afterglow. Furthermore Kaplan (106) found that the fourth positive group of nitrogen could be excited by passing a weak discharge through already active nitrogen. This would suggest that there exist in the active gas some metastable molecules which are easily raised to the higher energy levels from which the fourth positive group is known to originate.

Ewart and Rodebush (142) introduced hydrogen bromide into a flowing stream of glowing active nitrogen. At the point of mixing, the afterglow became a brilliant orange of greatly increased intensity. Further downstream the luminosity ceased and ammonium bromide was found, and a liquid-air trap still further along the tube contained free bromine. With hydrogen iodide the same sort of phenomenon took place with even greater intensity, and the flame beyond the point of entrance of the hydrogen iodide was of a brilliant blue color. Hydrogen chloride produced no increased luminosity but simply destroyed the afterglow.

The explanation of this behavior as given by the above authors is as follows: The ordinary afterglow involves bands originating from the eleventh vibrational level of the B state of nitrogen molecule and ending in the seventh to ninth level of the $A^3\Sigma$ state. The orange flame observed with hydrogen bromide consists of strong bands in the region 5900–6000 Å, probably corresponding to jumps from B_9 to A_6 or A_7. If the B_{11} nitrogen molecule could transfer two units of its vibrational energy to the hydrogen bromide molecule the resulting emission would be of the color observed. This vibrational energy transfer seems quite possible since the vibrational levels of hydrogen bromide are about equal to two vibration levels of the B nitrogen molecule. Ewart and Rodebush stated that the chemical changes undoubtedly involved atomic nitrogen. A reasonable mechanism would be:

$$\mathrm{N + HCl \rightarrow NH + Cl - 5\ Cal.;\quad N + HBr \rightarrow NH + Br + 15\ Cal.;}$$
$$\mathrm{N + HI \rightarrow NH + I + 35\ Cal.}$$

Although the heats of reaction are only approximate it is clear that hydrogen chloride should act differently from the others, since its reaction with nitrogen atoms is endothermic. The further reactions downstream would probably be:

$$\mathrm{NH + HBr \rightarrow NH_2 + Br;\quad NH_2 + HBr \rightarrow NH_3 + Br;}$$
$$\mathrm{NH_3 + HBr \rightarrow NH_4Br}$$

The disappearance of the afterglow below the point of entrance of the hydrogen bromide must be due to its catalytic destruction by ammonium bromide.

The blue continuous afterglow was attributed to a fluorescence of iodine. Later Rodebush and Spealman (143) decided that the orange glow with hydrogen bromide was not due to bromine bands. The orange glow was due to the first positive afterglow bands of nitrogen.

Kaplan and Cario's theory. A new idea regarding the constitution of active nitrogen was presented by Kaplan and Cario (107). They said that the long life of active nitrogen, which may be many minutes, precluded the possibility of only metastable molecules being present. The idea of an atomic constitution was much more rational when the long life of the glow was considered. The behavior toward wall catalysts also pointed in the same direction. However, metastable molecules may be formed later from the atoms. But in order to account for all the varied phenomena of active nitrogen they supposed that metastable atoms were also produced. These metastable atoms excite the metastable molecules, by collision of the second kind, to the energy levels of the first positive band group. Collisions between the metastable atoms (2.37 or 3.55 e.v.) (108) and the metastable molecules (8 e.v.) can just raise the molecules to an energy of about 11 e.v. of the sixth and eleventh vibrational state of the alpha bands (*B* level, see Fig. 70).

$$\iota = 0,\ 6.2\ \text{e.v.}) + \text{N}(^2P,\ 3.6\ \text{e. v.})$$

$$,\ n = 11) + \text{N(normal)}$$

$$\iota = 0,\ 6.2\ \text{e.v.}) \qquad 2.4\ \text{e. v.}) \rightarrow$$

$$\text{N}_2(\text{B}^3\Pi,\ n = \qquad \text{N(normal)}$$

If it be assumed that the metastable molecules are destroyed by heat and the metastable atoms are not affected, the experiments of Willey can be interpreted, for now two species are involved. Kaplan and Cario performed experiments where they destroyed the visible afterglow by heating and then showed that this dark glowless modification of nitrogen could still excite the D lines of sodium.

Further proof for the presence of atoms in active nitrogen was obtained by Herzberg (109), who found atomic nitrogen lines in the electrodeless discharge used for the production of the afterglow, when the discharge was obtained under conditions that produced the glow. If, however, the discharge was so modified that the afterglow could not be obtained, then the atomic nitrogen lines were absent. The atomic lines were in the infra-red (7000–8000 Å) and belong to the arc spectrum of atomic nitrogen. The presence of these arc lines was, however, a necessary but not sufficient condition for the production of the afterglow. The tube may be in such a condition as not to produce the afterglow, though the atomic lines were present in the original discharge. Herzberg found a similar situation in a tube with electrodes. So far then the conditions of the glow producing discharge are: (1) the red and infra-red arc lines of atomic nitrogen must be present; (2) the second positive band and perhaps the fourth positive group of molecular nitrogen must appear; (3) a peculiar intensity distribution, with high values of vibrational quantum number of greater intensity, must be shown. These conditions can be fulfilled in a discharge having comparatively high-speed electrons, like a condensed discharge. Once more Herzberg showed that only the bands of the first positive group occurred in the afterglow and that bands of the second positive group did not appear (Ruark, Kaplan, Okubo and Hamada).

Herzberg summarized the findings to date and concluded that the atomic constitution is more reasonable than the idea that metastable molecules are present only in active nitrogen. The points in favor of atoms are: (1) the long duration of the glow; (2) the catalytic influence of the wall; (3) the atomic lines in the producing discharge; (4) the lack of absorption of glowing nitrogen in the range 2000–8500 Å; (5) the peculiar distribution of the alpha band and the relation of the heat of dissociation of nitrogen to the term values of the favored eleventh vibrational band.

The points against the metastable theory are: (1) metastable molecules of sufficient long life are not known; (2) the second positive group is also found with mild excitation when there is no afterglow, in spite of favorable wall conditions. However, Herbert, Herzberg, and Mills (152) found an upper limit of 1/6000% for the stationary concentration of metastable atoms in active nitrogen. On the basis of the theory of Cario and Kaplan this would mean a lifetime of metastable ^2P atoms $\leq 8 \times 10^{-14}$ sec. The concentration of metastable molecules ($A^3\Sigma$ state) must be greater than 1/330%. But Frost and Oldenberg (151) could not detect metastable molecules of nitrogen in an electrical discharge, when using very powerful spectrographic equipment.

Against the atomic hypothesis is only Bonhoeffer and Kaminsky's (77) failure to obtain a more intense afterglow while increasing the pressure of the ordinary nitrogen. This rise in intensity is to be expected from the triple collision theory. Since it was not found, a difficulty for the atomic view arises. However, the experiments may not have been successful. The fact that some observers have obtained the second positive group of nitrogen bands may be explained by supposing that they really leaked into the afterglow from the producing discharge. Why, however, a second weak discharge should extinguish the afterglow (Strutt, Willey) is not so easily understood on the atomic basis but may perhaps be explained by the idea of metastable molecules.

Otherwise it is difficult to understand on either theory why the heat of dissociation of nitrogen does not agree more closely with the energies transferable to other systems by active nitrogen. Another observation shown earlier (Strutt) and repeated by Herzberg, namely, that the intensity of the alpha band was displaced toward the ultraviolet on lowering the temperature, has as yet no explanation.

A difficulty for the single atomic theory arose when Gaviola (110) suggested that the heat of dissociation of nitrogen is about 9.00 e.v. as Herzberg (111) pointed out, but the more complicated views of Cario and Kaplan may still be held and Birge (112) noted that one normal atom and one metastable atom (2.4 e. v.) have enough energy (9.0 + 2.4 e.v.) to produce the alpha bands in the eleventh vibration level. A rather direct determination of nitrogen atoms was made by Kenty and Turner (113), who showed by electron-impact experiments that nitrogen atoms could be formed by 10.8 volt electrons. They determined the atoms by adsorption on metals. In active nitrogen, metals are similarly covered by layers of atoms. At least it is fairly well established that atomic layers are readily adsorbed on metal surfaces. However, the proponents of the " metastable-molecule-only " theory are still active, and Kichlu and Basu (114) believe that the variation of life length with pressure is in favor of the view of metastable molecules in active nitrogen. But Lord Rayleigh (115) has pointed out again that his early experiments (23) showed clearly that collisions are important because compression momentarily brightens the glow considerably.

Evidence for nitrogen atoms. Moreover, Wrede (116) showed by direct pressure measurement that active nitrogen had several per cent of atoms under the usual conditions of production. Large-capacity discharges could be produced wherein the concentration of nitrogen atoms was as high as 40%. However, the discharge itself produces a mechanism which removes atoms so that ordinarily a smaller concentration is reached. These direct pressure measurements were made in a two-compartment tube. The discharge tube proper was one of the compartments, and a small hole separated the other section from the discharge tube. A mixture of atoms and molecules diffused from the discharge tube, whereas by means of proper catalysts the situation is so arranged that molecules diffused only outward from the second compartment and into the discharge tube. At the steady state a pressure difference was established which measured the concentration of the atoms in the active nitrogen gas. These experiments are as direct a proof of the existence of atomic nitrogen in the active gas as can be expected.

But spectroscopic methods also were finally devised which showed the presence of atoms in active nitrogen. Bay and Steiner (117) applied an additional high-frequency discharge external to the condensed discharge which produced the active nitrogen. This additional discharge brought out the atomic arc lines of nitrogen. They found independently of Wrede (116) that increased capacity in the producing discharge caused the atom concentration in the active nitrogen to increase. By using two additional discharges they could let the first one produce a lessened glow and under these conditions the second discharge showed the atomic lines fainter. This experiment showed that a fainter afterglow contains fewer atoms. They give their results in a very convenient form, which helps greatly to obtain a clearer picture of a complicated situation, as is seen in Table 22.

TABLE 22

SPECTRA IN NITROGEN DISCHARGES

Z. Bay and W. Steiner, Z. Elektrochem. **35**, 736 (1929)

Primary discharge producing active N_2		Additional weak discharge downstream	
Type	Spectrum	Negative glow	Positive column
None	....	No arc lines	4th positive group. NO bands strong
Uncondensed 300 milliamp. Positive column	1st and 2nd positive group strong. NO band strong. 4th positive group absent. No arc lines	No arc lines or only faint	4th positive group 50% stronger. NO bands weakened
Condensed o.5μf	Main intensity in the negative group. Spark lines of N^+. No NO bands. 4th positive bands present. Strong arc lines of N	Strong arc lines	4th positive group again weaker. NO bands disappeared.

Various experiments. In his further study Willey (118) found that pure non-glowing nitrogen showed no chemical activity, though it had been through a discharge, but nitrogen which exhibited the afterglow retained its chemical activity downstream though it had lost its luminosity further upstream. Needless to say, these experiments were carried out in a flow system. He also found that wall effects were of great importance, in agreement with Herzberg, and that the triple-impact hypothesis was evidently of great help in explaining the glow. He believed now that the glow-producing and chemically active species were certainly connected and adopted Kaplan and Cario's picture:

$$N + N^*(2.3\text{ e.v.}) + N_2 \rightarrow 2N_2 + h\nu \text{ (afterglow)}$$

where the N* atomic species may be the chemically active form. This mechanism accounted for the third-order decay of the afterglow and hence for the negative temperature coefficient. It indicated that the concentrations of the glow-producing and chemically active species were comparable; it provided an entity (N*) of 2.3 e.v. energy postulated earlier.

Further chemical studies involving active nitrogen were made by Tiede and Chomse (119), who investigated the action of agitated mercury and of atomic hydrogen. In the first experiments with mercury it was known that a nitrogen-containing substance (Hg_3N or HgN_3) was produced which yielded ammonia when treated with water. They found that nitrogen made glowless by additional discharge had no chemical activity towards a mercury surface. The yield was found proportional to the duration of the experiment, and they noted that a non-condensed discharge gave no active nitrogen able to react with a mobile mercury surface. From the work of Wrede (116) and Bay and Steiner (117) it was known that very few atoms were present in the gas. However, metastable molecules are then abundant and they showed therefore no chemical activity towards mercury. When the discharge contained a larger condenser it was able to produce a greater concentration of atoms. The reactivity of the gas was increased. In their study of atomic hydrogen reacting with active nitrogen they found, as Lewis (90) had, that both gases have to be activated in order to obtain any ammonia. They further noted that a carbon containing boron nitride was very sensitive toward active nitrogen and, as the latter contained fewer atoms, the " phosphor " showed less luminescence. Tiede and Knoblauch (141) obtained mercurous nitride (Hg_3N) and gallium nitride (lower than GaN). In 1% amalgams of potassium, sodium, lead, antomony, zinc, and cadmium only the mercury reacted. Lithium amalgam and a sodium-potassium alloy (5 : 1) yielded reaction products. Ammonia formation was also studied by Steiner (120), who found that activation of both hydrogen and nitrogen led to ammonia formation. However, he further obtained hydrazine from nitrogen atoms and hydrogen molecules. The hydrazine yield was relatively much smaller than the ammonia formed, and so earlier investigators did not find it. The probable steps in the mechanism of ammonia formation are

$$N + H + X \rightarrow NH + X' \qquad (1)$$

and in the hydrazine formation

$$+ X'' \qquad (2)$$

where X is a third body needed to remove the energy. The idea that triple impacts are necessary in these mechanisms was tested by Dixon and Steiner (121). They activated both gases and caused them to meet on a catalyst surface (Fe, Ni, Cu, Zn). The possibility of triple impacts was enhanced by the presence of " the wall " (the catalyst), and greater ammonia yield resulted. The formation of hydrazine is slower, however, in the heterogeneous case than in the homogeneous reaction. The most satisfactory mechanism is

$$N + H + (\text{Wall}) \rightarrow NH \qquad (3)$$

followed by

$$NH + H_2 + (\text{Wall}) \rightarrow NH_3 \qquad (4)$$

since the wall hastens the recombination of hydrogen atoms with a consequent reduction in their concentration. The reaction

$$NH + H \rightarrow NH_2 \qquad (5)$$

is reduced in frequency leading to a lower hydrazine yield.

Another point of interest mentioned by Dixon and Steiner concerns the reaction of metastable nitrogen molecules with hydrogen atoms. The afterglow is completely extinguished when atomic hydrogen and active nitrogen meet on the metal surface, whereas if molecular hydrogen and active nitrogen pass over the catalyst the afterglow is still visible for some distance beyond the metal surface. General experience and Kaplan-Cario theory teach that the afterglow disappears only when nitrogen atoms are removed, for if hydrogen atoms were reactive towards the metastable molecules, further amounts of this species could be formed beyond the catalyst from the atoms presumably present, and the gas would be expected to glow downstream from the catalyst. The fact that it does not glow shows that hydrogen atoms do react with nitrogen atoms and not with metastable nitrogen molecules.

Dixon and Steiner further found (122) that the ammonia formation was proportional to the concentration of hydrogen atoms as demanded by equation 3, provided that plenty of nitrogen atoms were present. However, an attempt to show the presence of NH radicals by spectroscopic means failed, which may mean only that their stationary concentration was too low or that the condition for their excitation was not favorable.

Ammonia is known to affect the afterglow, and they found that decomposition does happen to a slight extent; hydrazine is formed, however, only to the 1/250 extent of the ammonia decomposition. The most likely reaction seems to be

$$N + N + NH_3 \rightarrow NH_3^* + N_2 \tag{6}$$

$$NH_3^* \rightarrow NH_2 + H \tag{7}$$

Other bimolecular reactions with high activation energies seem less likely to occur. The metastable nitrogen atoms are also rather inactive. However, the activation energies of many processes considered are not known accurately, so that the complete picture of what happens when ammonia comes in contact with active nitrogen is not known. But the fact that nitrogen atoms are removed by ammonia molecules accounts for its quenching properties.

Metastable atoms. From the physical side a welcome result was the finding of metastable atoms by Jackson (123) and Jackson and Broadway (124). They performed a Stern-Gerlach experiment on active nitrogen and obtained visible evidence of the existence of nitrogen atoms in active nitrogen. The atoms were discovered on a film of silver nitrate with which they reacted, leaving a trace, which in the usual manner of these magnetic experiments was interpreted to indicate the presence of nitrogen atoms in the $^2P_{1/2}$ state. No other trace was found, showing that other species such as metastable molecules, etc., do not react as readily with silver nitrate. These findings strengthened the views of Cario and Kaplan considerably.

Further evidence of the importance of impacts of the second kind in the production of the afterglow was obtained by Kaplan (125), who observed spectra of the first positive group of nitrogen, with intensity distribution very similar to the afterglow, in uncondensed discharge of mixtures of nitrogen and mercury vapor at 5-cm. pressure. Collisions of the second kind between excited nitrogen molecules in the C levels, which are abundant in the discharge, with normal mercury atoms would produce excited mercury atoms (2^3P) and nitrogen molecules in the A levels, from which the alpha bands are emitted. These experiments showed that impacts of the second kind are plentiful in such discharges, which is a very interesting point. Kaplan (126) further obtained active nitrogen in an uncondensed discharge, which is unusual but depends according to his experience upon the conditions of the wall. The tubes had to be run two weeks before they assumed the state favorable for these experiments.

Another group of investigators convinced themselves that active nitrogen does not depend on electrical charges for its properties. Willey and Stringfellow (127) found that removal of charged particles has no effect upon the chemical reactivity of active nitrogen towards nitric oxide and presumably on its general chemical behavior. The earlier experiments of Constantinides (75) were confirmed, namely, that the electrical conductivity of active nitrogen is due to emission of electrons from metals. However, the emission is now shown to be due not to photoelectric action, but to impacts, for interposition of a thin quartz surface stopped the effect. The emission seemed to be due to impact of 8.0 e. v. metastable molecules upon the electrode surface.

It will be remembered that Kaplan was able to excite the auroral green line in oxygen using active nitrogen as the activating agent. Chhabra and Luthra (128) proposed to test Kaplan's theory by attempting to produce the similar forbidden transition ($^2D \rightarrow {}^2S$) in sulfur (λ = 6300 Å) by means of metastable atoms in active nitrogen. They caused active nitrogen to mix with sulphur vapor downstream, but they could not find the desired line. However, it may be that the forbidden line of sulphur is not so easily excited by active nitrogen as the similar line in oxygen. The authors recognized this situation, of course, and their experiments do not prove or disprove the presence of metastable atoms in active nitrogen.

As was mentioned earlier, the whole scheme of energy levels of the nitrogen molecule has not been completely developed in the sense that the *A* level which is a metastable triplet state is not known with any accuracy. It was taken to be "about" 8.2 e.v. above the normal state. Now it appears that Vegard (129), who has studied the luminescence of solidified gases, found the need of a state for his solid nitrogen spectra of 6.19 e.v. above the normal. Furthermore he mentioned the fact that Rudberg (130) found that electrons can lose 6.8 → 7.0 e. v. of energy to nitrogen molecules. If these states are all identical with the *A* state, the whole system of energy levels must be lowered by about 2 e. v. But then the original scheme of Sponer again becomes possible, for, with a dissociation energy of 9 e. v., the initial state of the alpha bands can be reached. The eleventh vibration state of the *B* level has now a value of 9.5 e. v. It is easy to understand why Okubo and Hamada can obtain mercury lines of term value 9.51 e. v.

Further work on active nitrogen was carried out by Okubo and Hamada (131). They now claim that pure nitrogen in the active state has the same energy after heating, and that the new dark modification of Kaplan and Cario, which they surmised formed after heating, does not exist. They obtained the same spectrum of mercury from the dark modification (i.e., which had been heated to 600° C.) of active nitrogen as when they used for excitation ordinary non-heated active nitrogen, and the highest energy level excited was 9.51 e. v. in either case. Nor do they find that a second discharge kills the glow and leaves the chemical activity, as Willey found. The nitrogen was allowed to act on a very sensitive thermocouple, and glowing nitrogen caused an effect on the thermopile proportional to the glow intensity. When a second discharge produced a glowless stage in *pure* nitrogen, the couple is not affected. Only when glowless impure nitrogen was flowing rapidly through the auxiliary discharge and over the thermocouple did the couple show an effect. This was ascribed to the invisible afterglow of the beta and gamma bands but not to pure nitrogen. It appears then that the pure active nitrogen loses its activity simultaneously with the quenching of its luminosity.

Since the second positive and the fourth positive bands of nitrogen are always prominent in condensed discharges, which also furnish active nitrogen abundantly, it has been assumed that the appearance of these bands in the producing discharge is connected with the mechanism of production. However, Hamada (132) found that the fourth positive group need not be present in a discharge which still would give active nitrogen, and he stated that bombarding electrons of velocity equal to the ionization potential of molecular nitrogen would produce the alpha band of active nitrogen. This situation points towards another process of formation of active nitrogen. The first step consists in the production of molecular ions. They decompose into atoms of nitrogen and then do their part in acting as active nitrogen. In the usual process of production of atoms it is implied that the excited nitrogen molecules in the B and C states dissociate into atoms on impact. The same author (133) found that spectral lines are not enhanced though their term values are equal to 2.36, 3.56 or 8.2 e. v. These energy values correspond to the levels of metastable nitrogen atoms in the ^2D or ^2P states respectively and to metastable nitrogen molecules in the $A^3\Sigma$ state. Such resonance enhancement was not observed, and it must be concluded that these species were present in active nitrogen in only very small concentration. In general, lower energy levels are excited by active nitrogen preferentially, and this state of affairs has to do with the nature of triple collisions between two nitrogen atoms and the metal atoms. The whole available energy (9.5 e. v.) will be distributed as follows: The newly formed nitrogen molecule will keep some of its vibrational energy; the excitation of the atom takes another fraction, and the remainder will go into kinetic energy of the interacting particles.

On the basis of their experiments Okubo and Hamada (134) evolved another idea of the nature of active nitrogen. They made two assumptions: The normal state of the nitrogen molecule ($X'\Sigma$), the eighth vibrational metastable A state ($A^3\Sigma$, $n = 8$) and the sixth vibrational B state ($B^3\Pi$, $n = 6$) have the same near-nuclear turning points (1.1 Å), and hence metastable molecules in the A state ($A^3\Sigma$, $n = 7$ or 8) are quite abundant in active nitrogen besides normal molecules and normal atoms. Okubo and Hamada would like to develop a theory of active nitrogen which does not involve the metastable atoms of Kaplan and Cario. However, the production of the alpha bands would require triple collisions on Okubo and Hamada's theory:

$$N_2\ (X'\Sigma,\ n = 0) \rightarrow N_2\ (A^3\Sigma,\ n = 7 \text{ or } 8)$$

$$N_2(A^3\Sigma, n = 7 \text{ or } 8) + 2\,N \rightarrow N_2(X'\Sigma, n = 0) + N_2(B^3\Pi, n = 6 \text{ or } 11)$$

$$N_2(B^3\Pi,\ n = 6 \text{ or } 11) \rightarrow N_2(A^3\Sigma,\ n\ =\ n) + h\nu(\alpha \text{ bands})$$

and the production of the afterglow would not be a bimolecular process. It is not so easy to see on this theory as it is on Cario-Kaplan theory how the ($B^3\Pi$, $n = 11$) state should be so prominent. Furthermore, the existence of metastable atoms has been shown by the Stern-Gerlach experiment. Okubo and Hamada (145) further studied the effect of inert gases and again hold that, although atoms are present in active nitrogen, they need not be metastable. They (146) also claim that the primary production of mole ions (N_2^+) is essential to the formation of active nitrogen. Whereas Okubo and Hamada differ in their view of the nature of active nitrogen from Cario and Kaplan, Arakatsu and Kimura (147) find that their experiments on the activation of air are best explained by the theory of Cario and Kaplan. An interesting review concerning active nitrogen appeared by Mund (149), and Hamada (150) discussed further the question of metastable molecules in active nitrogen.

Duration of the afterglow. Earlier investigators (17, 64) were able to produce the nitrogen afterglow of about 15-min. duration. From past experience it was to be expected that a large vessel with conditioned wall would be advantageous for a long-lived glow. In a 22-liter Pyrex flask prepared with a stem about 2 meters long and 70 mm. in diameter Knipp (137) was able to obtain, in tank nitrogen, by electrodeless high-frequency discharge, an afterglow of very long duration. The flask was flashed three times (duration of flash about 0.1 sec.) after the initial flash with the results shown in Table 23. The flask was not baked out, and it required about one year to produce the afterglow of longest duration. But even longer durations of afterglow were ob-

TABLE 23

AFTERGLOW IN ACTIVE NITROGEN
C. T. Knipp, Phys. Rev. 39, 181 (1932)

	Total interval, days	Duration of afterglow, minutes
Apr. 10 (1930)......	0	35
Aug. 12 (1930)......	122	110
Mar. 4 (1931).......	324	187
Oct. 28 (1931)......	563	165

tained by Lord Rayleigh (139), who studied the catalytic activity of the walls of the reaction vessel. Large glass bulbs wetted with sulphuric or metaphosphoric acids allow the glow of active nitrogen to remain for more than *6 hours!* He also studied the law of decay of luminosity and finds it dependent upon the material of the wall. The increase in luminosity noted at the very beginning of research on active nitrogen was investigated photometrically with the result that the law of luminosity decay seems to be a bimolecular reaction in which the excess of neutral nitrogen molecules has no part. This would mean that triple collisions involving neutral nitrogen molecules are not involved in the light-producing reactions.

Further evidence for metastable molecules. By conditioning the walls of the experimental tube Kaplan (138) and Jones and Grubb (140) were able to produce a strong afterglow in nitrogen by an uncondensed discharge. The first negative bands of nitrogen (due to $N_2{}^+$) were produced in the exciting discharge itself, indicating that the condition of this discharge simulated the auroral conditions where these negative bands are found. A very strong flash was observed at the beginning of the afterglow showing a high concentration of active material in the discharge itself. Kaplan considered the excitation of the $N_2{}^+$ bands to be due to the large concentrations of metastable nitrogen molecules in the $A^3\Sigma$ state. He further reported (138) the visual observation, in the strong afterglow, of bands arising on the very high vibrational levels (B_{18}) of the $B^3\Pi$ state. The afterglows reported to date consisted of bands mainly from the B_{10}, B_{11} amd B_{12} levels.

Technical use of the phenomenon of the nitrogen afterglow. It has happened many times, of course, that an apparently definitely theoretical problem has found its technical application. The phenomenon of the nitrogen afterglow has been suggested by Eltzin (136) as a means of determining the purity of gas mixtures which are used for the filling of commercial lamps. These lamps are filled with a gas mixture of argon (86%) and nitrogen (14%). Small traces of oxygen and water vapor are very harmful to the life of the lamps. The purity of the gas mixture used can be tested by observing the afterglow. When the gas is free from the above-mentioned impurities, it will not show the afterglow.

At present the nature of active nitrogen is still a problem for discussion. It cannot be said that the exact nature of this remarkable phenomenon is known. The great complexity of the situation in electrical discharges is well illustrated by this particular case. The most important information needed is the term value of the metastable ($A^3\Sigma$) state and the heat of dissociation of nitrogen. Even in the latest investigation on the band spectrum of nitrogen, Coster, Brons and van der Ziel (135) had to *assume* the value of 7.8 e. v. for the ($A^3\Sigma$) state, which is equivalent to the *assumption* that the heat of dissociation of nitrogen molecule is 9.0 e.v. However, the study of this problem is most fascinating, and it shows the great complexity of reactions possible in electrical discharge, the importance of impurities and the effect of wall reactions on the reaction complex as a whole.

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CHAPTER XIII

OXYGEN, OZONE AND COMPOUNDS OF ELEMENTS WITH ATOMIC NUMBER GREATER THAN EIGHT (8 TO 82)

(8) **Oxygen and ozone.** It is impossible within the confines of this book to review the enormous literature on the formation of ozone from oxygen. For the general aspects of ozonization one is referred to Chapter II and to the special treatises devoted to the subject.

In the present section some of the special aspects of ozonization and the more modern work on active oxygen are discussed.

In 1872 Houzeau (1) described an apparatus which he used to produce ozone; it belongs to a type designated by the present authors as a semi-corona tube. It consists of a metallic rod electrode in the axis of a cylindrical glass tube surrounded by a conducting liquid which serves as the other electrode as in the ordinary ozonizer. He obtained 60–120 mg. of ozone per liter of air at 15° to 30° C. In the same year Thenard used an all-glass ozonizer embodying the principles of several others. Owing to the failure of the glass wall under electrical discharge he wet the wall with antimony trichloride. He obtained great increases in the yield of ozone over those obtained in the Houzeau apparatus.

In 1876 Berthelot (2) showed that the direction of the current has no influence on the rate of ozone formation. A little later (3) he was unable to confirm the claim of Schönbein that ozone combines with nitrogen in the presence of alkali, but he did find nitrous compounds to be formed during the slow oxidation of phosphorus by air. In 1877 Berthelot demonstrated the thermal formation of ozone from oxygen (4).

In 1884 Figuier (VII, 7) demonstrated the activity of oxygen toward various substances under the influence of silent electrical discharge. Sulphur gave sulphur trioxide, selenium the dioxide, tellurium negative results. Chlorine was oxidized to chloric acid, bromine to bromic acid and iodine to iodic acid. Hydrogen chloride was also oxidized to chloric acid; nitric oxide to the dioxide; acetic acid to carbon dioxide and water; sodium formate to carbonate and oxalate. Warburg (5) in similar experiments in glow discharge found that lead monoxide is oxidized to the dioxide in oxygen at 5 mm. pressure.

With hydrogen instead of lead the reaction was reversed to produce metallic lead. Nitrogen gave negative results. (A series of erroneous interpretations led Warburg to believe that the reactions in electrical discharge are photochemical in nature caused by light emitted from the electrodes. Since the effect could not be transmitted through glass, he believed them due to the short ultraviolet.) Nevertheless he found that the rays (electrons) could cause chemical decomposition. He used both direct and alternating current.

In 1901 Berthelot (VII, 52) showed that when oxygen is sparked over mercury an oxide film is formed on the mercury. He claimed ozone to be intermediate to the reaction.

Warburg (6) found that both low temperature and luminous discharge were favorable to ozone formation. Warburg and Leithäuser (XI, 18) studied the influence of water vapor on ozonization in silent discharge. It is unfavorable in oxygen, more so in air and more so in both, the greater the distance from the electrode at which the discharge becomes luminous. At 80° water vapor had little influence on oxygen at constant pressure but in air it diminished the yield. (See also Chapter II.)

Pohl (IX, 11) studied the yield of ozone in the Siemens tube. Faraday's law is not applicable to the current yield. Instead of 96,500 coulombs per chemical equivalent only 360 to 1000 coulombs were required. The general interpretation given by Lind to this failure of Faraday's law for electrolytes when applied to chemical action in electrical discharge has been presented for the decomposition of water vapor in (1.8). The energy yields were 21–46 grams of ozone per horsepower-hour. The yield increases with pressure but is diminished by moisture. The maximum yield was attained at 6500 volts on the secondary circuit.

Anderegg (7) producing ozone from dry oxygen in corona discharge found that the ozone equilibrium is independent of current from 1.25 to 7.5×10^{-4} amp. According to Ray and Anderegg (X, 25), ozone formation in an ozonizer is probably not directly connected with the oxidation of carbon monoxide.

Assuming ozonization to be a process of dissociation of oxygen and that the amount of ozone formed is a direct measure of the primary dissociation, Warburg (IX, 21) compared the efficiency of the reaction $O_2 \rightarrow 2O$ with $NH_3 \rightarrow NH_2 + H$ in both the electrical and photochemical reactions. He calculated that one electron ("ion") in traversing the discharge tube dissociates four times as many oxygen as ammonia molecules. One unit of electrical energy decomposes three times as many oxygen as ammonia molecules, while one unit of radiant energy of 2070 Å absorbed caused the photolysis of nine times as many oxygen as ammonia molecules.

Anderegg (8) showed that ozone production in high-frequency (above a million cycles) discharge in an aluminum tube with gold or platinum central wire is subject to the same laws as in low-frequency discharge or in direct-current corona. In the corona 15 to 17 grams of ozone were produced per kilowatt-hour of gross input. Seventy to ninety moles of ozone were produced in air to one of nitrogen pentoxide. In the corona, sparking favors the oxidation of nitrogen over ozonization.

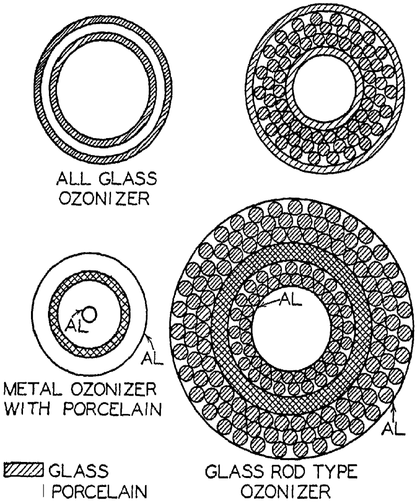

Fig. 71.—Types of ozonizers used in chemical investigations. McEachron and George, Purdue Univ. Expt. Station, Bull. 9 (1922).

McEachron and George (9) made an economic study of the production in air of ozone and oxides of nitrogen in various types of electrical discharge including Siemens tubes, rod-type tubes of metal, single dielectric tubes (semi-corona [Fig. 71]) and spark discharge. They discovered that the products of previous runs modify subsequent discharge. Increase of current raises the yield of both ozone and oxides of nitrogen to a maximum. Increase of pressure to about atmospheric increases the yield. The yield of nitrogen pentoxide increases with pressure in the spark and decreases in the rod tube (in the absence of sparking). Increased gas flow raises the production of nitric oxide and of ozone to a maximum. The corona favors ozone; sparking favors nitric oxide.

Fischer (10) investigated the conditions of ozone production in Tesla discharge. Oxides of nitrogen were detectable but very small in quantity. The production of ozone diminishes with increasing distance between electrodes. The concentration of ozone diminishes with increasing flow. Also using Tesla discharge Daniels, Keene and

Manning (11) found that short exposures give better than long ones. The molar ratio of ozone to nitric acid varied from 16 to 2.4. Uniform blue corona is fav pink streamers to nitric acid, sparking destroys ozone and does not greatly enhance nitric acid. Of the total energy supplied to the oscillating circuit of the Tesla system 45% is dissipated as heat. The chemical efficiency is limited to a few per cent of the energy supplied.

Briner and Susz (12) in seeking the "true" ozone yield in silent discharge obtained 246 grams per kilowatt-hour, or an energy yield of 20%.

Brewer and Westhaver (I, 15) found that ozone formation in the positive column of glow discharge is independent of pressure in the range 0.3–15 mm. but is proportional to the power input for low gas pressure and low current density. Ozone formation at maximum efficiency is proportional to the number of positive ions formed. One mole of ozone is formed by energy expenditure of 11.9 e.v. or 150 grams per kilowatt-hour. Therefore the yield $M_{O_3}/N_{\text{ions}} > 1$. *No evidence was found of ozonization caused by oxygen atoms or by radiation.* Foreign gases diminish ozone formation in the order $N_2 > A > He$. Helium gave a small increase.

In electrodeless discharge Schumb and Hunt (VII, 26) oxidized nickelous oxide to the black nickelic oxide and confirmed the oxidation first discovered by Thomson (IX, 95) of magnesium monoxide to the dioxide (MgO_2).

In glow discharge Henry (XI, 42) showed that, starting with an oxygen pressure of 7 mm. and freezing out ozone as formed, the dynamic equilibrium $3O_2 \leftrightarrows 2O_3$ is reached at 0.4 to 0.5 mm. Increase of current density accelerates the reaction, but less than in direct proportion. Ozonization occurs in the positive region rich in ions and excited atoms at 21.2 volts and at 8.9 volts due to excited molecules (Brewer and Westhaver (I, 15)) but not in the negative region rich in electrons. Metallic particles from the cathode cause catalytic decomposition of ozone on the wall. The nature and shape of electrodes have no influence, but small diameter of the vessel is favorable.

Zalogin and Nechaeva (13) show that the total yield of ozone increases with the velocity of air flowing through the ozonizer, but its concentration diminishes directly with velocity. (This is in agreement with the results for ozonization in streaming oxygen past an alpha-ray bulb (D'Olieslager [14]; Lind and Bardwell [15]) and is a direct consequence of the opposing deozonization in both instances.)

Glockler and Wilson (V, 18) and Nekrasov and Stern (V, 32) have demonstrated that pure oxygen disappears in electrical discharge in proportion to the area of the electrodes and walls, according to the latter, while the former have measured and interpreted the threshold voltages as follows. They find gas disappearance independent of electrons and evidently due to activation of oxygen by the hot filament. But besides such gas removal there appears further activation of oxygen due to electron bombardment. In the low-voltage region (3 – 8 e.v.), metastable oxygen molecules ($^1\Sigma_g{}^+$) serve as the activated state; in the region from 8–12 e.v., electronically excited molecules ($^3\Sigma_g{}^-$) are the activated species; and above the ionization potential (12.5 e.v.) ions ($O_2{}^+$) are formed and contribute to the drop in pressure by further reaction and consequent adsorption on the surface.

(8.16) **Oxygen-sulphur compounds.** Buff and Hofmann (VII, 39) sparked sulphur dioxide and produced the reaction

$$3SO_2 \rightarrow S + 2SO_3$$

which was confirmed later by Sainte-Claire Deville (IX, 2) and by Berthelot (VII, 52).

De Wilde (IV, 43) combined sulphur dioxide and oxygen in the Siemens tube to form sulphur trioxide.

Berthelot (VII, 48) decomposed sulphur dioxide into the elements in silent discharge, and two years later (X, 4) carried out the reaction:

$$2SO_3 + O \rightarrow S_2O_7$$

Excess of oxygen is favorable. The reaction is reversible, and an equilibrium is attained. In this research Berthelot announced for the first time the principle of the simultaneous reactions of decomposition and polymerization in electrical discharge. As examples he cited the reactions of hydrogen sulphide, phosphine, methane and carbon monoxide.

Losanitsch (VII, 55) carried out the following reactions in silent discharge:

$3SO_2 \rightarrow S + 2SO_3$ (as found by others in sparking, loc. cit.)

$SO_2 + 2H_2 \rightarrow 2H_2O + S$

$SO_2 + 2H_2S \rightarrow 2H_2O + 3S$

Moser and Isgarischew (II, 16) observed the following reactions in silent discharge:

$2SO_2 + O_2 \rightarrow 2SO_3$ (readily and solely) (stoichiometric mixture) (*a*) $4SO_3 + O_2 \rightarrow 2S_2O_7$ (without decomposition of SO_3) (in excess O_2)

(*b*) $3SO_2 \rightarrow S + 2SO_3$ (in excess SO_2)

Haber and Klemenc (16) used a gas-to-liquid discharge system with a platinum plate in the liquid and a silver or platinum electrode in the gas phase at reduced pressure. Sulphuric acid solution which constituted the liquid phase was oxidized to form both Cario's acid (H_2SO_5) and persulphuric acid ($H_2S_2O_8$) regardless of the direction of the current. The oxidizing agent was believed to originate or be activated in the gas phase. Hydrogen in excess of Faraday's equivalent was liberated. Klemenc (17) later confirmed this non-equivalence.

Meyer, Bailleul and Henkel (18) studied the reactions of sulphur trioxide in silent discharge and claimed to produce the tetroxide (SO_4) among other oxides of sulphur.

Schwarz and Kunzer (IX, 77) treated sulphur dioxide with chlorine and with bromine in the Siemens tube with the results:

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2; \quad SO_2 + Br_2 \rightarrow \text{no reaction}$$

Mahant (19) studied the reaction $2SO_2 + O_2 \rightarrow 2SO_3$ in electrodeless discharge. The rate is at maximum in the mixture 60% SO_2 and 40% O_2. The frequency of discharge has no influence. No thiosulphates or polythionates were formed. Oxygen subjected to this discharge oxidizes sulphur dioxide outside the discharge, but sulphur dioxide does not behave thus toward oxygen.

Zalogin and Nechaeva (13) determined that the yield of sulphur trioxide in the oxidation of the dioxide in high-frequency discharge decreases linearly with the increase of the sulphur dioxide content; it also decreases almost linearly with increase in the stream velocity and increases with the concentration of water vapor. The formation of sulphur trioxide and that of ozone are influenced similarly by various factors. Kolodkina and Nechaeva (20) continuing the study of sulphur trioxide formation, found that the yield is increased by higher current density at the same power input. By decreasing the gas velocity and the content of sulphur dioxide, oxidation to sulphur trioxide up to 98% was obtained. However, it did not appear practical to reduce these factors below the point at which 65–70% yields were obtained.

Joshi and Sharma (21) subjected sulphur dioxide to potentials of 4 to 16 kv. between calcium chloride and sodium chloride solutions serving as electrodes. The gas pressure falls, rapidly reaching equilibrium in 1 to 2 hours. The final mixture contains approximately 10% of unchanged sulphur dioxide, some trioxide and oxygen and two unidentified solids. After equilibrium is reached increase of voltage does not alter the pressure. Golyand (22) claimed the procedures and calculations of Kolodkina and Nechaeva to be in error. The validity of these criticisms was denied by them (23).

(9) **Compounds of fluorine.** Buff and Hofmann (VII, 39) failed to decompose silicon tetrafluoride by the arc, spark or hot coil of iron or platinum.

Berthelot (X, 4) stated that the fluorides (and chlorides) of boron and the fluorides of silicon are not changed by silent discharge (effluve), and later (24) that the perfluoride of sulphur is also stable. But he found (VII, 52) that the trifluoride of phosphorus is decomposed into phosphorus and pentafluoride of phosphorus which like the trichloride of sulphur is stable in the effluve. But most of the other gaseous compounds of fluorine are decomposed by the spark. In 1906 Berthelot (X, 22) found that fluorine and nitrous oxide do not combine in the effluve.

Ruff and Zedner (25) could find no evidence of combination of fluorine with nitrogen, oxygen or chlorine in the flaming arc or in the induced spark. But Ruff and Menzel (26) produced the oxide of fluorine (O_2F_2) in electrical discharge with electrodes 12 cm. apart in the gas mixture at 15–20 mm. pressure.

(11) **Sodium compounds.** Newman (27) found that the use of sodium or potassium as anode or cathode caused the absorption of nitrogen gas. The quantity of nitrogen absorbed per unit of current increased as the pressure of nitrogen was diminished. There was no effect of temperature up to 200° C., above which the absorption increased. A silvered bulb was used.

Kunsman and Nelson (28) showed that oxides of sodium or potassium on an iron anode cause hydrogen to disappear from the gas phase in electrical discharge. There is no reaction in the gas phase itself, only on or within the material used as source of the alkali gas ions (artificial spodumene).

(12) **Magnesium compounds.** It has already been mentioned in (8) that Thomson (IX, 95) discovered that magnesium oxide (MgO) is oxidized by oxygen in electrodeless discharge to a new oxide which was shown to be the dioxide MgO_2 hitherto unknown. The reaction was later confirmed by Schumb and Hunt (VII, 26), who also showed that magnesium unites with nitrogen in electrodeless discharge to form a nitride of magnesium.

(13) **Aluminum compounds.** De Hemptinne (VIII, 43) tried without success to reduce aluminum oxide by hydrogen in electrical discharge.

Goldstein (IX, 26) described the "catalytic" effect of argon in mixtures with nitrogen in promoting the formation of aluminum nitride by cleaning the aluminum surface and causing it to fuse (presumably under bombardment of argon ions) in condensed electrical discharge.

(14) **Silicon compounds.** For silicon fluoride see fluorine (9).

(15) **Phosphorus compounds.** Kohlschütter and Frumkin (IX, 74) found that glow discharge converts phosphorous vapor into red phosphorus which deposits on the wall in layers.

Moldenhauer and Dörsam (XI, 5) discovered that discharge between aluminum plates in the vapor of white phosphorus converts it into the red variety, which has such a low vapor pressure that it will not react with nitrogen.

Yajnik, Sharma and Bhatnagar (X, 40) converted red into yellow phosphorus in electrodeless discharge, but proved that phosphates are stable in it. Thomson (IX, 95) found that nitrogen and phosphorous vapor unite very rapidly in electrodeless discharge. Lodge (29) discovered the clean-up of nitrogen by phosphorus in the incandescent light bulb.

(16) **Sulphur compounds.** Maisin (30) repeated Berthelot's (VII, 48; VIII, 2) experiments with sulphur dioxide and oxygen in silent discharge. Contradicting Berthelot but in accord with Meyer (18), Maisin found no heptoxide (S_2O_7) but did obtain an oxide (S_3O_{11}) which seemed to be a definite compound though Meyer regarded it as a mixture of oxides.

The formation of nitrogen sulphides by Moldenhauer and Zimmermann (XI, 6) has been described in (7).

Schwarz and Royen (VII, 27) polymerized sulphur vapor at 460° C. in electrodeless discharge and observed contraction indicating the reaction $3S \rightarrow S_3$.

Kolodkina (31) determined that the decomposition of hydrogen sulphide is a first-order reaction in high-frequency discharge in the temperature range -15 to 18° C. The rate is temperature dependent. Polysulphides are formed which partially decompose on the wall into hydrogen and sulphur.

(17) **Chlorine compounds.** Davy (32) could obtain no evidence of the dissociation of chlorine in the electric spark. Berthelot (X, 4) likewise found chlorine and also bromine to be unchanged in silent discharge. Later Berthelot (VII, 52) decomposed the oxides of chlorine in the spark. Comanducci (VIII, 39) was able to synthesize chlorine

monoxide, Cl_2O, in silent discharge but found no reaction between chlorine and carbon monoxide.

Besson and Fournier (33) examined the reactions of a few gases containing chlorine in silent discharge, especially with hydrogen, and obtained the following reactions:

$$2POCl_3 + 4H_2 \rightarrow P_2O + 6HCl + H_2O; \quad S_2Cl_2 + H_2 \rightarrow S_2 + 2HCl$$

$$4SOCl_2 + 3H_2 \rightarrow S_2Cl_2 + 2SO_2 + 6HCl; \; 2SO_2 + 6S_2Cl_2 \rightarrow SO_2Cl_2 + 2SOCl_5 + 11S$$

Briner and Durand (VIII, 8) determined that, between −35 and −78° C., the polymerization of chlorine, if any, is less than 1/2000.

Schaum and Feller (34) used silent discharge to distinguish between the photochemical activation of chlorine and its electrical activation according to Venkatarmaiah (64). Chlorine which had passed through the discharge was distinctly more active toward benzene, acetic acid and toluene, and phenylmethyl alcohol ($C_6H_5 \cdot CH_2OH$); yields of 22–28% of the flowing chlorine were obtained.

De Hemptinne (VII, 17; VIII, 43) observed the reduction of the following compounds of chlorine by hydrogen in silent discharge: mercurous and mercuric chlorides, chlorides of silver, lead and tin, ethane hexachloride and potassium chlorate. Mahant (35) found that solid potassium chlorate is decomposed in electrodeless discharge to chloride but no chlorite nor perchlorate was formed. Yajnik, Sharma and Bhatnagar (X, 40) exposed potassium perchlorate to electrodeless discharge and got the following decomposition by stages:

$$KClO_4 \rightarrow KClO_3 \rightarrow KClO \rightarrow KCl$$

Willey and Foord (36) could detect no change of volume in the activation of chlorine in silent discharge, nor was its absorption spectrum altered perceptibly. But there was increased yield of hydrogen chloride on passing chlorine which had been activated either by the spark or by silent discharge into water. There was also enhanced reaction on aqueous solution of ferrous sulphate, but none for ferrous chloride and none with solution of oxalic acid, whereas increased reaction was shown toward acetic acid only when the chlorine was sparked. There was no increase toward methane, hydrogen or dyes, but there was increased reaction with toluene and a definite increase with benzene. An impurity, probably hydrogen chloride, favored the reaction. No decision was made as to the active form of chlorine.

(18) **Argon.** Over a period of five years beginning soon after the discovery of argon, Berthelot (VII, 52; X 45, 46) spent a prodigious

amount of effort in attempting the fixation of argon by combining it with a variety of organic compounds mostly in the gaseous state, by subjecting them when mixed with argon to silent discharge. It is surprising in how many instances he found positive evidence of fixation. It is at least clear that he did attain removal of argon from the gas phase in many instances. Probably it was simply occluded and carried down with the condensed liquids or solids. He claimed a positive result with benzene and with carbon bisulphide, negative ones with acetylene, fluorine, ethylene, glycolic ether, acetaldehyde, acetone, pentane, petroleum ether, pentamide, ethyl cyanide, and ethylsulphocyanide. Berthelot reported the following percentages of argon fixed: with benzene, 3–6%; toluene, 2–3%; cymol, 6%; turpentine, 2%; anisol, 1–2%; phenylsulphocyanide, 2%; phenylcyanide, 5.3%; aniline, 1–2%; phenol, 2–3%; benzaldehyde, 1–2%. With a number of other organic compounds the results were uncertain. The degree of fixation is seen in the relative amounts of different gases removed by carbon bisulphide:

$$2CS_2 \text{ to fix } 1H_2; \quad 4CS_2 : 1N_2 \quad \text{and} \quad 34CS_2 : 1A$$

The fixation of nitrogen was found to be greater in the aliphatic than in the aromatic series; the reverse was true for argon.

Fischer and Iliovici (37) could find no evidence of compound formation of argon with hydrogen, titanium, tin, lead antimony or bismuth in electrodeless discharge. The spark between cadmium and aluminum electrodes gave condensation products all of which showed spectral evidence of argon, but it was concluded that only absorption was responsible.

Lind and Bardwell (38) found that the rare gases were carried down by cuprene precipitated from acetylene by alpha rays in proportion to their atomic masses. The interpretation was suggested that the positive ions of the rare gas atoms act as clustering centers and that upon ion recombination the heavier gases escape more difficultly from the neutralized cluster. Complete recovery was effected by moderate heating without decomposing the cuprene at all. Probably a similar explanation is applicable to all the other cases cited here for different types of electrical discharge.

Goldstein (IX, 26) ascribed catalytic properties to argon in facilitating the clean-up of nitrogen as Al_2N_3 in induction discharge. According to him, argon has the function of cleaning the aluminum surface and causing it to melt, which makes nitride formation rapid. Possibly both effects are due to bombardment by argon ions.

Ruff and Menzel (39) were unable to confirm the combination of argon with fluorine, or of krypton with fluorine, in electrical discharge as reported by Antropoff (40).

(19) **Potassium compounds.** Bose (41) bombarded the surface of a concentrated solution of potassium hydroxide with electrons accelerated by electrodeless discharge from a Tesla coil. Instead of the reactions to be expected from the formulation:

$$K^+ + E^- \rightarrow K \quad \text{and} \quad 2K + 2H_2O \rightarrow 2KOH + H_2$$

he obtained an explosive mixture of oxygen and hydrogen (excess of hydrogen) in 2000 fold excess over the requirement of Faraday's law. He explained this by the dissociating action of highly energetic electrons and the faster diffusion of hydrogen than of oxygen from the solution. (Also some peroxide may be formed in solution.)

De Hemptinne (VII, 17; VIII, 43) obtained very slight reduction of potassium chlorate by hydrogen in silent discharge.

Newman (27) showed the absorption of nitrogen by potassium or sodium, when used as anode or cathode in electrical discharge.

Using voltages up to 565 volts, Kunsman and Nelson (28) found that no reaction takes place in the hydrogen gas phase but only in or on the surface of the solid potassium (or lithium) ion source.

(20) **Calcium compounds.** Bhatnagar, Sharma and Mitra (42) observed the decomposition of calcium sulphate to sulphite in electrodeless discharge. Thomson (IX, 95) showed that calcium oxide is oxidized to the dioxide in electrodeless discharge similar to the reaction of magnesium oxide in oxygen.

(22) **Titanium compounds.** Böck and Moser (43) found that the reaction of titanium tetrachloride and hydrogen in silent discharge gives hydrogen chloride and a solid mixture containing titanium trichloride. Continuing the same experiments, the production of two forms of titanium trichloride was claimed, a brown form having heat of solution of 48,493 cal. and a violet form showing 45,043 cal.

(25) **Manganese compounds.** De Hemptinne (VII, 17; VIII, 43) studied the reduction in electrical discharge of solid compounds of manganese by hydrogen and by carbon monoxide. Manganese dioxide was readily reduced by both. Potassium permanganate was not reduced by hydrogen.

(26) **Iron compounds.** The magnetic oxide (Fe_3O_4) was reduced by hydrogen in effluve (VII, 17; VIII, 43).

(28) **Nickel compounds.** No reduction of nickel oxide (NiO) by hydrogen in effluve could be observed (VII, 17; VIII, 43).

(29) **Copper compounds.** The reduction of cupric oxide (CuO) by hydrogen in effluve was found to proceed at a moderate rate (VII, 17; VIII, 43).

(30) **Zinc compounds.** Oxidation of zinc oxide by oxygen in electrodeless discharge to form a peroxide was observed by Thomson (IX, 95) to take place but at a slower rate than in the case of magnesium oxide.

(33) **Arsenic compounds.** Berthelot (VII, 51) found both arsine (AsH_3) and stibine (SbH_3) to be readily decomposed in the electric spark. Smits and Aten (IX, 10) observed strong synthesis and decomposition of arsine in the ozonizer. The decomposition and a weaker synthesis were also found for stibine.

According to Besson and Fournier (44) the action of the effluve on hydrogen and the chloride of arsenic leads to the formation of a polyarseno-chloride ($As_{11}Cl$), the formula of which they regarded as doubtful. The formation of a subchloride, however, was assured by selective solubility in carbon tetrachloride.

De Hemptinne (VII, 17; VIII, 43) obtained some reduction of arsenic trioxide by hydrogen in effluve. Thomson (IX, 95) effected the synthesis of arsine in electrodeless discharge.

(34) **Selenium compounds.** Kramer and Meloche (45) have shown that selenium is oxidized to dioxide and trioxide in the negative glow of glow discharge in oxygen. A larger proportion of the trioxide was found behind the electrodes than elsewhere in the tube.

Rheinboldt, Hessel and Schwenzer (46) effected the direct synthesis of selenium trioxide for the first time by exposing selenium and oxygen to discharge of high (radio) frequency. On dissolving the trioxide in water both selenous and selenic acids were formed. If the tube is tapped so that selenium trioxide comes into contact with selenium during the reaction a deep green product analogous to green $SeSO_3$ or to blue SSO_3 was obtained.

(35) **Bromine compounds.** In 1887 Thomson (47) gave the results of experiments with bromine and iodine vapors in the spark and in silent discharge as judged by the increase of pressure. Iodine was dissociated and returned to normal pressure quite slowly; bromine appeared to be less dissociated and returned very rapidly to normal. He interpreted this to indicate a greater dissociation of iodine than of bromine, and a more rapid recombination of bromine atoms. Kropp (48), however, disproved Thomson's claim of the dissociation of iodine in the spark.

Canfield and Hayes (49) found that hydrogen bromide is dissociated to the extent of 50% in silent electrical discharge at 33° C. and 10 kv., which corresponds to thermal equilibrium at 2800° K. This is comparable with the results of Moser and Isgarischew (II, 16), who found 15.8% of dissociation of carbon dioxide corresponding to 2500° K. and 0.6% dissociation for hydrogen chloride corresponding to 2000° K, while Davies (IX, 15) found ammonia dissociated to the extent of 97.2% corresponding to only 900° K.

Bhatnagar, Sharma and Mitra (42) observed that potassium bromate is dissociated in electrodeless discharge to potassium bromide and potassium hypobromite (KBrO), which was confirmed by Mahant (35).

Schwarz and Kunzer (50) could find no reaction between bromine and oxygen in a Siemens tube but claimed that bromine alone produced a solid which did not react further. On the other hand, Lewis and Schumacher (51) formed a solid oxide of bromine $(Br_3O_8)_n$ at $-5°$ to 10° C. by the action of a several fold excess of ozone on bromine.

(46) **Palladium compounds.** Damianovich (52) asserted that helium at low pressure reacts with palladium volatilized from the cathode in electrical glow discharge. He claimed the product to be more stable than platinum helide having properties distinct from those of palladium or its hydride.

(47) **Silver compounds.** De Hemptinne (VII, 17; VIII, 43) found that silver chloride is very readily reduced by hydrogen in silent discharge. According to Cole (IV, 7), the blackening of photographic emulsion by low-speed electrons is due to the radiation caused by electron impact and is a discontinuous function of the speed. A film of fluorescing oil was found to increase the sensitivity greatly. Grain size and gelatin thickness influence the effect of 100 volt electrons.

(50) **Tin compounds.** Paneth (VII, 10) found that in order to form stannic hydride (SnH_4) by sparking between tin electrodes in hydrogen it is necessary to have a small amount of hydrocarbon mixed with the hydrogen. De Hemptinne (VII, 17; VIII, 43) was able to obtain only a fair reduction of stannous chloride by hydrogen in silent discharge.

(51) **Antimony compounds.** (See Arsenic compounds [33].)

(53) **Iodine compounds.** (See also bromine [35].) Klüpfel (53) found, on electrolyzing a solution of potassium iodide with one electrode in air above the solution, that iodine separated at the surface in Faraday equivalence. De Hemptinne (VII, 16) obtained only fair reduction of mercuric iodide by hydrogen in silent discharge. Potassium iodide was still more difficult, giving only doubtful results.

Warburg (II, 10) made a quantitative study of the synthesis of hydrogen iodide in the Siemens tube in a flow system. Hydrogen passing over iodine at various temperatures furnished mixtures with different concentrations of iodine vapor in a large excess of hydrogen. The rate of flow and potential were also varied. Steady state was attained at 8 moles of hydrogen iodide per mole of iodine. (This ratio, of course, would be expected to be quite different in absence of excess of hydrogen. About 3.3 to 9 molecules of hydrogen iodide were synthesized per electron flowing.) Schumb and Hunt (VII, 26) observed the synthesis of hydrogen iodide in electrodeless discharge.

Bhatnagar, Sharma and Mitra (42) showed that potassium iodate like the bromate is decomposed in electrodeless discharge to iodide and hypoiodite (KIO), which is to be contrasted with the result of Mahant (35) who obtained free iodine and oxygen also from the iodate in electrodeless discharge. According to Yajnik, Sharma and Bhatnagar (X, 40) the following successive reactions take place in electrodeless discharge acting on potassium periodate:

$$KIO_4 \rightarrow KIO_3 \rightarrow KI; \quad O_2 \rightarrow O_3; \quad KI + O_3 \rightarrow K_2O + I_2 + O_2$$

On this basis, one would interpret the free iodine obtained by Mahant as being produced by the secondary action of ozone on the iodide.

(78) **Platinum compounds.** Damianovich (55) demonstrated that helium is absorbed by platinum deposited by electrical discharge (sputtering) in helium, 14–34 cc. of helium per gram of platinum deposited. Microphotography showed structural differences indicating chemical combination, which evidence was supported by the observation of pressure drop of helium (56) and by X-ray powder spectrogram (57).

Schwarz and Kunzer (50) failed to find any enhancement of the catalytic activity of contact platinum after passage of electrical discharge in the gases involved in the two reactions of great industrial importance: the oxidation of sulphur dioxide to trioxide and the oxidation of ammonia to nitric oxide.

Damianovich, Piazza and collaborators (58) secured evidence for the formation of compounds between platinum and nitrogen, oxygen or helium when platinum is cathodically deposited. The formula of the oxide seemed to be Pt_2O_3. The main evidence consisted of the lowered density of platinum and its behavior toward aqua regia as well as sharp decomposition, at a well-defined temperature. Hydrogen under the same conditions does not form a compound. Piazza (59), continuing the investigation, asserted that the oxide of platinum formed on the platinum cathode by discharge in oxygen is similar to that prepared chemically except that it decomposes more completely at 600°.

(79) **Gold.** Asada and Quasebarth (XIX, 38) produced a type of sputtering by making copper foil containing gold the cathode in glow discharge in mercury vapor. The gold is selectively vaporized and completely removed before the copper is entirely disintegrated. Assuming zero concentration of gold at the copper surface, the diffusion coefficient is calculated as 10^{-6} cm.^{2} per day. (See also Haber, Jaenicke and Matthias [54].) The earlier claims (I, 7, page 223) for having produced gold by the electronic bombardment of mercury now appear in the light of modern knowledge of the nucleus so improbable that they are cited for convenience of historical reference only.

(80) **Mercury compounds.** De Hemptinne (VII, 16; VIII, 43) reduced mercuric oxide readily by hydrogen in silent discharge, also mercurous and mercuric chlorides, mercurous bromide and mercuric iodide. Yajnik, Sharma and Bhatnagar (X, 40) found that electrodeless discharge caused the conversion of red mercuric oxide into the yellow form which then decomposed into mercury and oxygen.

(82) **Lead compounds.** De Hemptinne (VII, 16) used the ready reduction of lead dioxide, by hydrogen in silent discharge, as a standard of rate comparison with other oxides reduced by hydrogen and also by carbon monoxide. The rate of reduction of lead monoxide is greater than that of the dioxide. Lead chloride gave a negative result.

Clark (60) failed to confirm the theory and experiments of Wendt and Grimm (61) on the effect of lead tetraethyl, which they thought caused the more rapid recombination of ions, and which they believed to have a bearing on the theory of anti-knocks in the internal-combustion engine. When Clark produced a steady source of ions in the hydrocarbon mixture by means of X-rays, there was no difference in the rate of recombination of ions whether the mixture contained lead tetraethyl or not.

Bhatnagar, Sharma and Mitra (42) produced the following reaction in lead compounds by means of electrodeless discharge:

$$PbSO_4 \rightarrow PbSO_3 \rightarrow PbS$$

$$PbSO_4 + Mg \rightarrow PbS + MgO_2$$

$$Pb(NO_3)_2 \rightarrow PbO_2 + 2NO_2$$

Prilezheava (62) examined the spectrum of the decomposition of lead tetraethyl in glow discharge after long exposure. Bands of methine (CH) appeared at 4300 and 3900 Å, also C_2 (Swan) bands, Balmer lines of hydrogen, mercury and lead lines and a continuous spectrum from 3600 to 2200 Å. Lead spark lines were absent, indicating no lead ions, and the arc spectrum of lead is emitted at the decomposition. Direct current was used, 10–15 milliamp. at 500–600 volts.

Various inorganic compounds. In an extensive series of investigations Miyamoto (63) reduced a large number of inorganic solids by means of hydrogen in silent discharge at 15,000 volts in a vessel cooled to about room temperature. Metallic sulphates yielded metallic sulphides and frequently hydrogen sulphide. Potassium, beryllium and magnesium sulphates were not changed. Metallic sulphides produced hydrogen sulphide. Nitrates were reduced to nitrites and nitric oxide and sometimes metallic hydroxides, frequently ammonium nitrate. Metallic chlorides formed hydrogen chloride and free metal. Hydrated cupric nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) yielded copper, cupric oxide, nitrogen dioxide, nitric oxide, ammonium nitrate and nitrite and free ammonia. Other metallic nitrates were changed to similar products. Perchlorate gave chloride and water; cyanides, hydrogen cyanide and free metal; sulphocyanides, hydrogen sulphide and cyanide; selenates, selenites and selenium; thiosulphates, free sulphur and hydrogen sulphide; selenites and tellurites, selenium and tellurium. Sulphur and iodine yielded hydrogen sulphide and iodide. Arsenic anhydride (As_2O_5) gave arsine, arsenic trioxide and water. Potassium ferricyanide was reduced to ferrocyanide and hydrogen cyanide. In exceptional cases only was reduction absent.

De Hemptinne's work (VII, 17) on the reduction of metallic oxides by hydrogen has already been cited under hydrogen.

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CHAPTER XIV

GENERAL TOPICS

General topics and methods. In 1863 Seguin (1) compared the induction spark with other types of electrical discharge and found no essential differences with reference to chemical effects. In the same year Boettger (X, 9) reported the color of the spark and some chemical behavior in a number of gases including hydrogen, carbon dioxide, methane, ethane, oxygen, carbon monoxide, hydrogen chloride, sulphur dioxide, ammonia, hydrogen sulphide and stibine.

Hempel (2) claimed that sparking ceases when a vessel containing nitric acid and copper turnings is brought below the spark gap. Sparking sets in again upon removal of the vessel and displacement of the brown fumes by air.

Houzeau (XIII, 1) in 1872 described an arrangement consisting of a glass tube with a central copper-wire electrode and external copper coil (semi-corona) with which he obtained 60–120 mg. of ozone per liter of air at 15 to $-30°$ C. Berthelot (VII, 42) found the tube of Houzeau superior to that of Babo in the formation of acetylene from other hydrocarbon gases. De Wilde (IV, 43) in 1874 described and made use of a Siemens tube without citation of other authorities. Berthelot (VII, 48) later described several forms of tube for silent discharge suitable for use over the pneumatic trough. P. and A. Thenard (VIII, 37) attribute the influence of water vapor, in reducing the yield of ozone in silent discharge, to the useless expenditure of electrical energy on water vapor (an explanation that would hardly accord with modern theories).

Perotti (3) controlled the rate of combination of explosive mixture of hydrogen and oxygen between 3 min. and 6 hours by regulating the current intensity in silent discharge; also by heating an interior platinum wire by light focused on it by a lens, and in the case of hydrogen and chlorine by screening from light by suitably thick layers of alum solution.

Although it is not related directly to electrical discharge it is interesting that Berthelot (4) in 1880 made some experiments on the chemical effects of high-frequency sound waves. Using a tube and wheel arrangement giving 7200 vibrations per second he obtained negative results in the decomposition of ozone, arsine, hydrogen peroxide, persulphuric acid and the combination of ethylene with concentrated sulphuric acid. He cited Noble and Abel, Champion and Pellet, and many others as having found that explosives are detonated by ultrasonic vibrations. Berthelot attributes their results to secondary effects.

In 1895 Thomson (5; IX, 84) passed electric discharge through tubes narrow enough to prevent diffusion. He claimed that, in hydrogen chloride, chlorine goes to the positive and hydrogen to the negative electrode, whereas in bromochloride (BrCl) chlorine goes to the negative electrode.

Wiedemann and Schmidt (IX, 83) showed that Faraday's law is not applicable to the decomposition in glow discharge of hydrogen chloride, mercuric chloride, bromide or iodide.

Berthelot (6) studied the best conditions of voltage and temperature for chemical reaction in silent discharge. Pohl (IX, 11) asserted that the displacement current in a Siemens tube contributes nothing to the chemical action and should be subtracted from the total current before making comparisons. He showed how to measure the displacement current alone by evacuating the tube.

De Hemptinne (IX, 16) demonstrated that in point-to-plate discharge in gaseous mixtures containing oxygen and a combustible gas the rate of oxidation is faster when the point is negative, especially for pressures below 20 mm. The reaction, he found, takes place in the luminous portion of the discharge and is caused by ionization. (This is probably the earliest claim that chemical reaction in electrical discharge is due to ionization.) Otto (7) investigated the influence of frequency in ozone formation.

Smits and Aten (IX, 10) determined the steady state in a number of gaseous systems in the ozonizer and in the mercury arc. They found displacement of equilibrium in favor of the endothermic reaction.

Besson and Fournier (VIII, 48) mentioned the use of a battery of ozonizer tubes arranged in series as to gas flow.

Wehnelt and Franck (8) measured the change of pressure in air (or nitrogen, which gave the same result) around the anode in direct-current discharge. Assuming Faraday's law, one-quarter of the ions are generated near the anode and three-quarters near the cathode. It appeared that the electrons stopped transporting molecules at about 0.136-mm. pressure. Chrisler (9) observed that the absorption of hydrogen and helium at anodes of sodium, potassium, mercury and glass follows Faraday's law for a short time.

In 1909 Warburg (II, 2) gave an extensive review of chemical effects in silent discharge in which he dealt with the inapplicability of Faraday's law and with the influence of current density, of pressure, of electrode separation, of temperature and of water vapor. He discussed the formation and equilibrium of ozone, the decomposition of ammonia, the oxidation of nitrogen, the yield of ozone and the characterization of silent discharge. His conclusion that the chemical effects may be photochemical in nature is one with which the writers cannot agree.

Makowetzky (IX, 17) found that discharge between a gas phase of nitrogen and oxygen to a water phase gives hydrogen, oxygen, hydrogen peroxide, nitric acid and ammonia.

Baker (10) asserted that the presence of water vapor is necessary for the combination of oxygen with hydrogen or with carbon monoxide under the influence of radium bromide (in an open tube). This is not in accord with the results of Lind (I, 7) for the same reactions caused by radon. Baker also claimed that carbon monoxide and oxygen combine more slowly thermally in an electrical field which removes ions. Strong (XI, 30) suggested a relation between gaseous ionization and chemical action. Briner and Durand (VIII, 8) recognized that the usual laws of kinetics, of mass action, and of heat of reaction do not apply to gas reactions in electrical discharge. They realized the importance of the current density and believed that the higher yield of ammonia in the presence of excess of hydrogen is due to its higher conductivity at the same pressure. This interpretation is plausible but in sharp contrast with the results of Jungers (11) in ammonia synthesis by alpha rays. But it is to be remembered that in the latter it is the low stopping power of hydrogen that reduces the amount of ionization and the chemical action, since the alpha particle has sufficient energy to pass across the entire gas phase, and is not dependent on the field and free path for its ionizing power. Briner (12) considered the electrical (ionic) versus the thermal theory for the combination of nitrogen and oxygen and cited the theory of Strong (XI, 30). The ion theory of the electrical reaction had been previously proposed by Lind (VII, 93), who pointed out that, if the reaction is due to ions which mostly recombine in the gas phase without reaching the electrodes and contributing to conduction, the chemical action would greatly exceed the Faraday (current) equivalence. This has been repeatedly confirmed experimentally by various authorities. In using the arc with auxiliary electrodes in the synthesis of ammonia and of nitric oxide, Briner (IX, 19) believed the reactions to be of thermal rather than electrical nature. Ehrlich and Russ (XI, 31) measured the electrical variables in the Siemens tube and the effect of ozone and of nitric pentoxide upon them. The Dolezalek electrometer was used for the current measurements. Both ozone and nitrogen pentoxide increased the arcing potential.

Skaupy (13) proposed the possibility of separating gases in the direct-current arc depending on the difference of their ionization potentials, using an inert gas as conductor. Of course, this was before the interchange of charge between ions by means of electron exchange had been established.

De Hemptinne (14) expressed the view that the addition or subtraction of electrons from atoms and molecules results in their chemical activation.

Yoshida (15) asserted as a result of his studies of Lichtenberg figures that the photographic effect is not due to direct electrical action as claimed by Brown (16). He attributes it wholly to the luminosity caused by recombination of ions. Therefore the figures map the paths of ionization.

Skaupy (17) investigated the clean-up of hydrocarbon impurities in discharge through the rare gases. He observed that the clean-up is rapid in neon leaving a spectrum of pure neon, but that in argon the clean-up is much slower. Skaupy, pointing out that the ionization potential of hydrocarbons lies between those of neon and argon, concluded that neon does not, but that argon does, trap the available electrons. This view should probably be revised as follows: to make the positive ions, not the negative ones, responsible for the clean-up. In excess inert gas, most of the positive ions will be Ne^+ or A^+, as the case may be. The free electrons will not have much tendency to be trapped by helium or argon atoms or by hydrocarbon molecules. The positive He^+ can ionize hydrocarbon molecules in collisions of the second kind by electron exchange: $He^+ + H.C. \rightarrow H.C.^+ + He$. The hydrocarbon ion is then removed by trapping at the negative electrode or in part by condensation and polymerization. But the A^+ ion, owing to its lower ionization potential, will not be able to remove electrons from the hydrocarbon molecules. Hence their only means of removal will be by being initially ionized by the current-carrying electrons. Since the relative concentration of hydrocarbons is low ("impurities"), this probability is small, consequently their removal in atmosphere of argon is slow.

For a comparison of the action of electrical discharge and light in decomposing ammonia and oxygen, refer to Warburg (Chapters II and IX.)

Montemartini (VIII, 4) employed a special type of direct-current corona, a metal thread 1 meter long in a glass tube, operating at 5–6 milliamp. to demonstrate a variety of gas reactions:

$${}_2 \rightarrow 2O_3; \quad 2CO_2 \rightarrow 2CO + O_2; \quad N_2 + 3H_2 \rightarrow 2NH_3$$

$$CO + H_2O \rightarrow CO_2 + H_2; \quad C_2H_2 + N_2 \rightarrow 2HCN$$

$$CO_2 + 2H_2 \rightarrow H\cdot CHO + H_2O; \quad C_6H_6 + CO_2 \rightarrow C_6H_5\cdot COOH$$

$$H_2S \leftrightarrows H_2 + S; \quad 2SbH_3 \leftrightarrows 2Sb + 3H_2$$

Daniels, Keene and Manning (XIII, 11) determined the chemical efficiency in ozone formation in corona discharge to be 1% of the total energy applied or 2% of the portion expended in the discharge tube.

Lind (VIII, 24) elaborated an ion theory of chemical action in discharge, assuming that ions form addition products (clusters) with neutral molecules before neutralization, which is the last stage of the reaction. Ions may recombine without any chemical reaction resulting, as in the case of carbon dioxide which is not measurably decomposed by alpha rays. But upon the introduction of a suitable "acceptor" such as hydrogen, the CO_2^+ ions react readily. Obviously the free electrons contribute nothing to the chemical action unless they have affinity for at least one species of molecule present.

Anderegg and Bowers (18) studied the effect of packing dielectric material around the central aluminum wire in a silent discharge tube. The production of ozone and nitrogen pentoxide in air was measured using fragments of glass, quartz, flint (blue and white), earthenware (bare and covered with beeswax), hematite and glass wool as contact substances. The yields were more dependent upon the nature and extent of the surface than on the inductive capacity of the packing materials. Glass wool was found to be especially active in the synthesis of nitrogen pentoxide. Anderegg (19) used a similar arrangement with glass rods and air. Anderegg and McEachron (20) proved that the fog formed when ozonized air is passed into an absorbing solution is caused by the hydroscopic nitrogen pentoxide and is not connected with the presence of ions.

Thomson (21) presented an extended discussion of the chemical behavior of gas ions. One of the important conclusions was that negative ions, when present, should be equally effective chemically with positive ions.

Peskov (22) found that the addition of heavy substances such as barium sulphate, colloidal solutions of platinum, bismuth hydroxide, stannic oxide has a sensitizing effect on action of X-rays in enhancing their reaction with diastase, the decomposition of *o*-nitrophenyl alcohol and other reactions.

George and Oplinger (23) determined the sparking potentials in oxygen, nitrogen and air, and the effect of interposing metal plates.

Becker and Rossenbeck (24) showed that the first effect of discharge in air in a Siemens tube is to cause a rise in pressure, gradual at first and then suddenly greater. Eventually the original pressure is reestablished. There is some wall adsorption.

Elliott, Joshi and Lunt (VII, 18) advanced the theory that chemical action in electrical discharge is to be related to excited rather than to ionized molecules. They proposed the equation:

$$\frac{k}{p} = \left(\frac{K}{e}\right)\left(\frac{P}{E}\right) \exp \frac{V_0}{lE}$$

k = reaction velocity constant; p = gas pressure; K = a constant; e = ionic charge; P = power consumed; E = field strength; V_0 = critical potential; l = ion mean free path.

Pisarzhevskii (25) attributes the catalytic activity of metals to the action of their free electrons on adsorbed gases. Also he suggests that the enhanced effect under radiation of the metal catalyst is due to photoelectrons.

Boutaric (26) classified the different types of electrical discharge in gases and assigned three causes of chemical reaction: thermal, ionic and photochemical activation. Discharge was classified as dark, silent luminous (effluve) and including glow and brush discharge, high-tension arc, low-tension arc, all capable of being the seat of chemical action.

Marshall and Nunn (27) investigated the degree of dissociation in air, hydrogen and chlorine in high-frequency discharge. It was small in the ozonizer, greater in a cylinder end-on. Ionization in air was greater than in hydrogen.

Finch (XX, 13) studied the cathodic slow combustion of hydrogen and of carbon monoxide in direct current between metal electrodes, in dry and in moist gases. The low tension arc (20 volts and a hot cathode) did not prove suitable for combustible gases, but the high-tension arc (cold cathode and several hundred volts) was satisfactory. Combustion occurred in three luminous zones, the cathode or negative glow, in the anode spot and in the positive column. The reaction in the last was not great and there was none in the Faraday dark space. Sputtering also occurred.

Rheinboldt and Hessel (X, 38) introduced substances between the condenser plates in high-frequency discharge in glass vessels immersed in oil. Only liquids or solids with some conductivity which can damp the resonance were effective. Carbon glows. Conducting liquids boil; conductivity water does not. A mixture of carbon monoxide and oxygen reacted at 20–30 mm. pressure.

Peters (28) classified all types of discharge and illustrated the use of each. Lind (29) compared the yield in photochemical and in radiochemical reaction. Lüdke (30) discussed the theory of activation and ionization by high-frequency discharge in rotating fields, assuming that any activated state will be obtained by the minimum expense of energy.

Yajnik, Sharma and Bhatnager (X, 40) exposed various solids to electrodeless discharge from a Tesla coil and compared the results with those for ultraviolet light, visible light and heat. The reactions which occurred in electrical discharge have been described in Chapter XIII, (17), (53), (80), (82). Phosphates, carbonates and oxalates were found to be stable.

Lechler (31) invented an apparatus to promote surface catalysis in gases by electrical discharge in such reactions as the oxidation of sulphur dioxide or the hydrogenation or chlorination of hydrocarbons.

Thomson (VII, 22) presented a theory of electrodeless discharge and some examples of chemical action under its influence.

Gubkin (32) examined the deposition of metals at the surface of electrolytes with one electrode (cathode) in the gas phase. With 1000 Planté accumulators he obtained metallic silver, copper and platinum (black), but zinc oxide instead of the metal.

Fischer and Peters (33) devised an apparatus for the decomposition in glow discharge by introducing the reacting gases near the electrodes and removing the products at a remote point in the flow system.

Coustal (34) observed the following phenomena in exposing phosphorescent sulphides on an insulated wooden plate in silent discharge at 200 kv. If initially luminous, the substances lost their luminosity with either charge on the plate but more rapidly when positive. Gradual recovery ensues when the discharge stops. If initially non-luminous, a slight luminosity is produced by the discharge.

Willey (VI, 146) found spectroscopic evidence for the existence of the free radicals CH, OH and NH in electrical discharge. CH radicals are found with any hydrocarbon; hydroxyl radicals in water vapor and mixtures of hydrogen and oxygen; and imid radical occurs in ammonia and mixtures of nitrogen and hydrogen. The yield of acetylene from a mixture of methane and excess of nitrogen is much greater in intermittent discharge from a special thyratron circuit than in alternating or direct-current discharge of the same voltage. The ratio of hydrogen cyanide to acetylene produced is increased with the frequency of discharge from the thyratron circuit.

Jovitschitsch (35) closed a long series of observations of deficiencies in the sum of hydrogen and carbon in the analysis of the products of the action of silent discharge on hydrocarbons by assuming that they are converted into oxygen by the addition of four hydrogen nuclei to the carbon nucleus. (Of course our present knowledge of nuclear reactions and of the energy necessary to produce such reaction would not allow the possibility of their occurrence under Jovitschitsch's conditions.)

Kuczynski (36) sought to apply Le Châtelier's principle to the reaction in electrical discharge as follows:

$$\ln(K_1/K_2) = [H^2/8nRT](v_2e_2 - v_1e_1).$$

K_1 = state of thermal equilibrium; K_2 = steady state in the electrical field; e = dielectric constant in each state; v = volume; H = field strength. Thus it would appear that the field favors formation of compounds with high dielectric constant, polymers and compounds with asymmetric linkages.

Engel (37) used the oscillograph to investigate the field strength, quenching pressure and minimum arcing voltage in the luminous arc.

Briner and Susz (38) calculated the maximum concentration of some endothermic compounds at higher temperatures: for the thermal formation of ozone only 276 parts per billion at 3750° K.; for formation of nitric oxide at 4000° K. they calculated 31.6% in a 1:1 mixture and 10.9% for the mixture $4N_2 : O_2$, all at 1 atmosphere pressure. Therefore the thermal effect should be negligible in the formation of ozone by electrical discharge methods and only minor in the synthesis of nitric oxide electrically.

Gedye (39) compared the quantum and ion efficiencies in the photochemical and electrical decompositions of ammonia, nitrous oxide, ozone synthesis and decomposition as follows:

Ammonia decomposition: quantum yield $< \frac{1}{2}$ ion pair yield (by alpha rays)
Nitrous oxide decomposition: quantum yield = ion pair yield = 4 (by cathode rays)
Ozone synthesis: quantum yield $\simeq$ ion pair yield = 3 (by alpha rays)
Ozone decomposition: quantum yield = 1–2 (chains of considerable length in alpha-ray and cathode-ray decomposition.)

Klemenc (40) has devoted attention to systems with one electrode in the gas, the other in the liquid phase. With glow discharge he observed unusual oxidation and reduction processes. With the cathode in the vapor phase the following reduction reactions occurred:

$HNO_3 \rightarrow HNO_2, NO, N_2O$

$Fe_2(SO_4)_3 \rightarrow$ reduced with difficulty

$KClO_3 \rightarrow$ reduced 90% with iron electrode

$KBrO_3 \rightarrow$ reduced 90%

$H_2CrO_4 \rightarrow$ reduced 88%.

$HClO_4 \rightarrow$ reduced slowly up to 40%

Using the same arrangement Klemenc and Hohn (41) showed that the amount of reaction exceeds the Faraday current equivalent. They assumed the initiation of chain reactions by short-wave-length radiation from the glow discharge. They found chloric and perchloric acids to be more readily reduced than in ordinary electrolysis.

Rummel (42) discovered that glow discharge at 4 microamp. and 6 kv. and an electrode spacing of 2.5 mm. could be stabilized, that is, be made uniform over the surface of aluminum electrodes 26 mm. in diameter, by covering them electrolytically with an oxide film.

Jolibois (43) asserted that the seat of reactions such as would occur at high temperature, for instance, the decomposition of hydrogen, nitrogen, oxygen or chlorine, is in the positive column. The synthesis of ammonia which occurs near the cathode he thought to be catalytic and due to sputtered metal.

Colloids. Miyamoto (44) found that a dilute solution of acid auric chloride ($HAuCl_4$) is reduced by hydrogen in silent discharge to form a gold sol which was stable even in the absence of protective colloid. A suspension of silver oxide (Ag_2O) in water was similarly reduced by hydrogen to a silver sol; chloroplatinic acid (H_2PtCl_6) to platinum sol, and palladium chloride ($PdCl_2$) in excess of hydrochloric acid to palladium sol. Gold and silver sols in ethyl, isobutyl and amyl alcohols were also prepared. Stable hydrosols of manganese dioxide were prepared from dilute solution of permanganate and hydrogen. Sols were not formed from suspensions of permanganate in isobutyl or in amyl alcohols. Hydrosols of selenium and tellurium were prepared by the same method but were not stable without the addition of gum arabic or gelatin before reduction. Organic sols of selenium and tellurium were not stable. Miyamoto further observed (45) the formation of colloids by hydrogen activated in silent discharge in heterogeneous systems as follows: hydrosol and alcosol of cuprous oxide from cupric sulphate; hydrosol and alcosol of cupric sulphide from cupric sulphide; hydrosol of mercury from mercurous nitrate; hydrosol of mercuric sulphide from mercuric sulphide and from mercurous sulphocyanide.

Vitamins. Askew, Bourdillon and Webster (46) passed a 0.05% alcoholic solution of ergosterol through a silica tube in the center of the positive column in glow discharge. Eighteen per cent of the ergosterol was transformed into a resinous mixture containing vitamin D equivalent to about 6% of the original ergosterol. When discharge took place through argon instead of air, 37% of the ergosterol was transformed. The vitamin D formed corresponded to 16% of the original ergosterol.

Insulation. Fleming and Johnson (47) discussed the failure of insulating windings which they attributed to the formation of ozone, nitrogen dioxide and nitric acid in air spaces. The high-potential leakage which occurs in such air spaces produces these highly active oxidizing agents which attack the organic winding material and gradually weaken or destroy it. Gealey (48) described the deterioration of oils used for insulation and gave specifications for oils to be used in transformers, switches, lightning arresters and feed regulators. Clark (49) discussed the properties of high-voltage gaseous dielectrics. (See Chapter IV.)

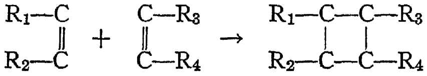
This problem of deterioration of electric power cable has become even more important because of the use of underground cables at higher voltages. The change in the insulation is noted by the appearance of a waxlike solid substance. This flaky solid material is called "wax X." It is formed at points of greatest electrical field and in itself seems to be a good dielectric and not harmful. However, its presence points to action due to the electric field, and it is now recognized that electron bombardment of gas contained in minute pockets within the insulating layer of the cable may lead to breakdown. Gas-free oils are not affected readily in electrical fields. Oxidation (by atmospheric oxygen) does not account for wax formation. These questions have been studied by various investigators, for example by Hirshfeld, Meyer and Connell (70) and by Wyatt (71).

Lubrication. The early experiments of de Hemptinne (VII, 15) in the reduction of oleic to stearic acid by means of electrical discharge through hydrogen at reduced pressure have been cited under hydrogenation in (1). Later (50) he described the conversion of olein to stearin by the same process with vertical iron plate electrodes wet with a thin layer of olein. The quantity of substance hydrogenated was not always proportional to the intensity of the current. For a given current density the quantity transformed is a maximum for a definite separation of plates for each pressure of hydrogen. (This is readily understood, in a qualitative way at least, in the light of modern ideas of discharge and the resultant ionization.) It was claimed that the viscosity of oils produced in this way has a smaller variation with temperature than the natural mineral oils have.

During the World War this process came into use under the name "voltol process" and was used to increase the viscosity of low-grade oils to make them suitable for use as lubricating oils.

Friederich (51) described an equipment for the treatment with glow discharge in 110 mm. of hydrogen at 4300 to 4600 volts, 60°–80° C.; 500 cycles; 19–23 amp. A viscosity of 100 Engler degrees at 100° C. was attained with the treated oil.

Hock (52) presented the scientific details and theory of the voltol process. Starting with a fish oil of average molecular weight 870, the molecular weight was raised to 1100 (half voltol). Mineral oil of molecular weight 400 was then added and electrical treatment continued until high viscosity is reached at an average molecular weight of 650 (full voltol). The hydrogen pressure is maintained at about 0.1 atmosphere. A theory attributed to Nernst assumes that polymerization results from the addition of two olefins to form a ring compound:



(Without denying that such reactions may take place, it is evident that they are incapable of explaining the larger part of the reactions occurring. They would be limited to a doubling. But Lind and Glockler (VII, 72) have shown that ethylene is readily condensed in the ozonizer to a liquid with average molecular weight at least five times that of ethylene, and that hydrogen evolution exceeds its combination. Also saturated paraffin gases can be similarly condensed to liquid by elimination of either hydrogen or methane. Obviously, neither are double bonds initially necessary nor is the condensation limited to a doubling when they are present.)

Eichwald (53) also described results using the voltol process. Tar oil in silent or glow discharge in hydrogen behaved similarly to the fatty oils. Oil containing 42% saturates and 58% unsaturates was converted to a liquid containing 69% saturates and 31% unsaturates with an increase of viscosity from 2.3 to 37.5 Engler degrees.

Later Eichwald (54) gave further data for the treatment of fatty oils in glow discharge in hydrogen. The viscosity rapidly rose to a point where further treatment was impossible. Mixtures of mineral oils yielded lubricants with low temperature coefficients of viscosity. Oleic acid was partly converted into stearic acid in atmospheres of hydrogen, nitrogen, air or carbon dioxide. In the absence of initial hydrogen, hydrogen was liberated from oleic acid itself.

Hock (55) claimed that solid products do not appear in the commercial operation of the voltol process. But in laboratory experiments gelatinous products separated from very viscous oil which proved to be insoluble in ether, benzene, chloroform, aniline, acetic acid, etc., but could be saponified by boiling with alcoholic solution of potassium hydroxide.

Becker (56) gave a theory for the voltol process stating that hydrogen is split off from hydrocarbons in silent discharge. The molecular residues then combine to form larger molecules and increase the viscosity. Similar action is possible in inorganic compounds. (This theory is substantially the same as proposed earlier by Lind to explain the polymerization or condensation of gaseous and liquid hydrocarbon under alpha radiation, except that he supposed that combination occurs first under the static influence of the positive molecular ions, and that splitting occurs upon ion recombination.)

Iwamoto (57) studied the reactions of various organic compounds in silent discharge. Cod-liver oil under discharge in hydrogen or nitrogen at normal pressure showed an increase in specific gravity and index of refraction but a decrease in iodine number. In hydrogen, complete deodorization was claimed after 1.5 to 3 hours *without* destruction of vitamin A. Oleic, linoleic and linolenic acids in hydrogen are polymerized and hydrogenated. In its absence, both reactions occur, but much more slowly, and polymerization exceeds hydrogenation since the hydrogen must first be liberated from the acid. In carbon dioxide or sulphur dioxide neither polymerization nor hydrogenation takes place. In oleic acid hydrogenation increases from 15 to 95° C. with voltage from 5 to 20 kv. The rate decreases with increasing spacing between the electrodes from 3 to 20 mm. under 10–20 kv., decreases with gas pressure from 0.006 to 10 mm. and increases with pressure from 100 to 600 mm. In saturated acids, capric, lauric, palmitic and stearic, the melting point is lowered, the index of refraction and specific gravity raised while saponification and neutralization values are diminished. An iodine number is produced in the originally saturated compounds. From solid acids, liquid polymers are formed. The action is attributed to the elimination of hydrogen to produce double bonds.

According to Rabek (58) increase of frequency decreases the time necessary for a given change in viscosity. By employing a 2 k.v. unit, at 7600 cycles an increase of 100% in viscosity was attained in a 10% vegetable oil. Blaschke (59) confirmed the results of Becker (56) and used the same hypothesis to explain them. Hock (60) made X-ray examinations of the products from various oils subjected to discharge but failed to find evidence of fibrous structure. The products after extraction with petroleum ether were stable to heat. In the presence of hydrogen sulphide the products became darker and of disagreeable odor. Evers (61) reviewed these reactions. In glow discharge, in liquid paraffins, he observed the evolution of hydrogen, increase of molecular weight and viscosity. In lubricating oils, discharge produced an improvement in lowering the temperature coefficient of viscosity. Cycloparaffins were found to etch the glass walls strongly.

Flames. It would be outside the province of this treatment to attempt to cover or even to deal in any extensive way with the phenomena of flame ignition or propagation. But certain theories have been put forward regarding the role of ions in flame propagation which should properly be considered.

It has long been known that gaseous ions are present in flames and render them electrically conducting. In 1910 Thomson (I, 2) made the hypothesis that electrons generated at the advancing flame front project themselves into and ionize the ignitible mixture and so activate it for propagation of the flame. Haber and Lacy (62) confirmed Davidson (63) and Tufts (64) in finding the inner cone of a Bunsen flame to be more highly conducting than the surrounding gases. Haber suggested that the gas ions in this region might be intermediate products in the reaction of combustion. A little later Lind's result with the slow oxidation at ordinary temperature of hydrogen, carbon monoxide and the hydrocarbons by oxygen under the ionizing influence of alpha rays suggested an experimental test of the necessity of electrons in flame propagation. On account of the negative nature of the results, they were not published until 1924 (65). The experiments consisted in igniting, at one end of a glass tube, electrolytic hydrogen and oxygen mixture at a pressure just a little higher than the ignition pressure to see whether its propagation would be prevented by allowing it to pass through an electrostatic field capable of removing electrons during its passage.

The choice of hydrogen was probably unfortunate. Malinovskiĭ and Lavrov (66) confirmed the finding that flame in hydrogen and oxygen is not inhibited by a field but in the case of mixtures of hydrocarbons and oxygen positive results were obtained. Bernatzkiĭ and Rotanov (67) extinguished flames in mixtures of 15% methane, 10% ethylene and 22.5% acetylene respectively with air at 900, 1400 and 560 volts. They do not agree with Haber's theory of the function of the positive ion.

Malinovskiĭ, Rossuikhin and Timkovskiĭ (68) found the inhibitive influence of alternating current to be one and a half to two times as weak as direct current in mixtures of acetylene with air at the same voltage. The difference between the two diminishes with decreasing concentration of acetylene in the mixture. The strongest effect was observed in the mixture containing 25% of acetylene.

Lewis (69) studied the influence of a longitudinal field on the propagation of flame in mixtures of air and various hydrocarbons. In all gases, and both with lean and rich mixtures, flame was extinguished when the downstream electrode was negatively charged. The flames of rich mixtures of methane or ethane with air are extinguished when the downstream electrode is negative; the flames of lean mixtures of these gases are not extinguished with this direction of field. But the flames of lean mixtures of propane, butane, isobutane, propene and butene are extinguished when the upstream electrode is negative and the flames of rich mixtures of these gases cannot be so extinguished. One concludes that flame speed is a function of the concentration of positive ions, hence the flame is invariably pulled toward the negative pole.

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PART III

THE PHYSICAL AND THEORETICAL ASPECTS OF DISCHARGE REACTIONS

CHAPTER XV

ELECTRON AFFINITY OF ATOMS AND MOLECULES

Introduction. Experiments on the conductivity of gases at low pressure, mobility measurements and the use of magnetic fields in the mass spectrograph fully confirm the view that both positively and negatively charged particles can exist in a gas under appropriate conditions. However, it is of interest to note whether there are other lines of evidence, perhaps more indirect in character, which point to the same conclusion. Especially is this question important when negative atom ions and mole ions are considered, for such negative ions are not found quite so readily in a mass spectrograph as the positive ions are. They are formed at higher pressure and they appear in discharge tubes (1) as a result of the interaction of neutral atoms and molecules with electrons or other particles. The *possible* existence of negative ions can, however, be deduced from general considerations of stability. If the view is adopted that a given structure (molecule or ion) is stable if in its formation a great deal of energy is liberated, then it can be shown that the atom ions of certain elements are stable structures and it may be expected that they can be formed under appropriate circumstances, as for instance in a discharge tube or a mass spectrograph. These considerations of stability are also applicable to atoms, and in this sense it may be said, for example, that the hydrogen atom is a stable structure as related to the proton and electron, for these latter two will readily combine to form the former and a large amount of energy is liberated as radiation or otherwise when the reaction

takes place. The ionization potential of hydrogen atom is a measure of the energy given out in this reaction, since it is the work necessary to separate a hydrogen atom into a proton and electron. In the same way it may be asked: Have the hydrogen atom and a second electron any tendency to form a stable hydride ion with one negative charge? The question can be put another way: Is the hydride ion stable? Is energy given out when a hydrogen atom and an electron combine, or is this reaction highly endothermic? In still other words: Has the hydrogen atom an electron affinity? By electron affinity is meant the energy given out when a system such as the hydrogen atom in the above example combines with an electron and thereby becomes a negatively charged hydride ion. The question whether atoms and molecules possess an electron affinity is of great importance not only as affecting their behavior in electrical discharge devices but also from the general point of view of molecular structure. In the case of some substances it is of importance to distinguish carefully between the electron affinity of atoms and molecules, as for example, hydrogen, oxygen, chlorine, etc.

$$\mathrm{Cl} + \mathrm{E}^- \rightarrow \mathrm{Cl}^-;\ \mathrm{Cl}_2 + \mathrm{E}^- \rightarrow \mathrm{Cl}_2{}^-;\ \text{etc.}$$

The following methods for the quantitative determination of the electron affinities have been proposed: calculations from a model by Bohr theory; extrapolation of Moseley curves of the ionization potentials of electronic sequences; calculations based on wave mechanics; thermochemical calculations based on a Born cycle using grating-energies of crystals; study of the thermodynamic equilibrium at high temperature; conductivity of flames; spectroscopic determinations; dissociation by electron impact; qualitative evidence; electron affinity of free radicals.

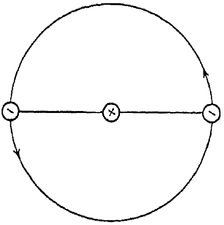

FIG. 72.—The hydride ion (H^-) on Bohr theory. Bohr, Phil. Mag. **30**, 394 (1915).

Bohr theory. Bohr (2) calculated the electron affinity of hydrogen atom for a model of hydride ion consisting of a proton and two electrons revolving in the same circular orbit of radius r (Fig. 72). The velocity of the electrons is v, their mass is m and their charge is e. The total energy W of such a system is

$$W = -\frac{2e^2}{r} + \frac{e^2}{2r} + mv^2$$

The mechanical and electrical forces must balance

$$mv^2 \qquad \frac{e^2}{r^2}$$

The quantum condition applied to the system demands that the angular momentum over one period of the motion be

$$2\pi m v r = n h, \quad n = 1, 2, 3 \cdots$$

where $\pi = 3.1416$, and $h =$ Planck's constant. From these considerations it is found that

$$W_n = -\frac{9}{4} \cdot \frac{\pi^2 m e^4}{n^2 h^2};\ W_1 = -\frac{9}{8} W_0$$

where $W_0 = 13.52$ e. v., which is the ionization potential of the hydrogen atom. The electron affinity ΔW of the hydrogen atom is found by considering the reactions:

$$\begin{array}{ll} H^+ + 2E^- \rightarrow H^-, & W_1 = +1.125 W_0 \\ \quad H \rightarrow H^+ + E^-, & W_0 = -1.000 W_0 \\ \hline H + E^- \rightarrow H^-, & \Delta W = +0.125 W_0 \end{array}$$

The electron affinity of the hydrogen atom is 1.69 e.v. or 38,900 cal., and the hydride ion is stable to this extent, because the last reaction above is exothermic.

This calculation is now of historical interest only, for it must give a wrong value for the electron affinity in the same sense that the calculated ionization potential of helium on the Bohr theory is 28.7 e.v. whereas the experimental value is 24.5 e.v. Pauling (3) thought to improve this calculation by determining the screening constant for a two-electron system from the known ionization potential of helium. He found the hydride ion unstable (−0.08 e.v.). However, his calculation can now be adjusted, for lately Edlén and Ericson (4) have determined the ionization potential of Li^+ and Be^{++} to be 75.28 and 153.15 e.v., respectively. It is then possible to find the variation of screening constant of a two-electron system with atomic number and to interpolate for the hydride ion. Such an empirical calculation made by Glockler (5) gives +0.66 e.v. for the electron affinity of the hydrogen atom. The hydride ion is a stable structure. Calculations of electron affinities of other atoms on the simple theory outlined above have not been made.

Extrapolation of ionization potentials. In the study of X-ray spectra of the elements it is well known that the square root of the frequency of certain X-ray lines is a (nearly) linear function of the atomic number (6). Since the electron affinity of an atom may as well be considered to be the ionization potential of the ion it is easily understood that it is related to the ionization potential of atoms of similar electronic structure. The structures

$$[^-,\ \mathrm{He},\ \mathrm{Li}^+,\ \mathrm{Be}^{++},\qquad \text{etc.}$$

are two-electron systems, and Bartlett (7) found an extrapolated value for the electron affinity of hydrogen of +1.4 e.v. However, a very long extrapolation is necessary since the ionization potential of helium is 24.5 e.v., ($\sqrt{24.5} = 4.95$). The calculation of Pauling mentioned in section 1 is equivalent and when adjusted for variation of screening constant as was done by Glockler (5) gives the value of + 0.66 e.v. Bartlett also finds values for the electron affinity of fluorine (+3.5 e.v.) and chlorine (+ 3.0 e.v.). The electron affinities of O^- (+2.2 e.v.) and S^- (+2.8 e.v.) have also been estimated by this method by Mayer and Maltbie as mentioned in section 4. The method considered here has been modified by Glockler (8), who considered the ionization potentials of isoelectronic systems as a parabolic function of atomic number. The calculations yielded estimates of the electron affinities of the first eighteen elements of the periodic table, and the values agree reasonably well with results obtained by other methods (Table 24; Fig. 73) where checks can be made.

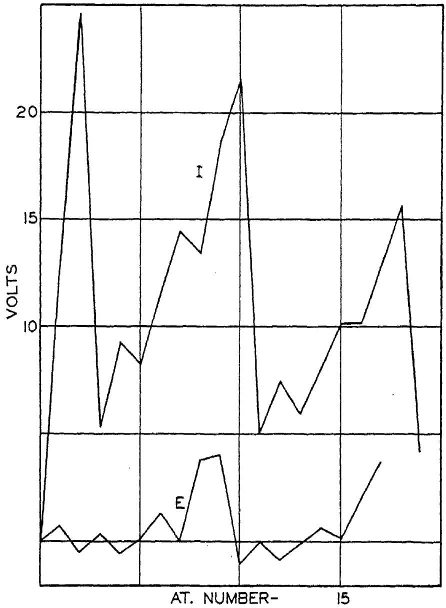

FIG. 73.—Ionization potentials (*I*) and electron affinities (*E*) of the light elements. Glockler, Phys. Rev. 45, 111 (1934).

TABLE 24

Electron Affinities of the Light Elements
G. Glockler, Phys. Rev. **45**, 111 (1934)

Atom	Electron Affinity	Atom	Electron Affinity
H	+0.76	Ne	−1.20
He	−0.53	Na	+0.08
Li	+0.34	Mg	−0.87
Be	−0.57	Al	−0.16
B	+0.12	Si	+0.60
C	+1.37	P	+0.15
N	+0.04	S	+2.06
O	+3.80	Cl	+3.70
F	+3.94	A	−(1.0)
Ni	+0.25	Ag	+0.95
Cu	+1.17	Hg	+1.79

Calculation by wave mechanics. The original quantum-theory calculation of Bohr can now be made on the basis of wave mechanics. The Schroedinger equation for two electron systems (H^-, He, Li^+, $^+$, B^{+++} etc.) is

where ∇_1^2, ∇_2^2 = second differential coefficients in respect to the coordinates of electrons 1 and 2; m = the mass of the electron; h = Planck's constant; E = the total energy of the system; Z = the atomic number of the nucleus; r_1 = distance of electron 1 from nucleus; r_2 = distance of electron 2 from nucleus; r_{12} = distance between electrons; ψ = the wave function of the system.

If this equation could be solved exactly, all the term values of the atomic system represented by it would be known for they are the "eigen-values" of the problem. However, only for the hydrogen atom has it been solved exactly and for others it can be solved only approximately. Hylleraas (9) calculated the ionization potential of helium by this method. Bethe (10) used the methods of Hylleraas and found the electron affinity of hydrogen to be +17 k-cal. or 0.74 e.v.

Hylleraas (11, 13) and Starodubrovskii (12) also made this calculation and obtained +0.700 ± 0.015 e.v. These calculations give the best value for the electron affinity of hydrogen, for the ionization potentials calculated similarly for He, Li^+ and Be^{++} check experimental values very well (14). The electron affinity of no other atom has been calculated so far by the methods of wave mechanics, because even for these two electron systems the approximate calculations are quite complicated. For atoms with more electrons these complications increase.

However a quantum-mechanical examination has been made of processes leading to the formation of negative ions. Massey and Smith (96) consider the following possibilities: direct electron capture, dissociation of molecules on electron impact, collisions of heavy particles, extraction of electrons from metals by atoms. They discuss these phenomena and they point out, for example, that an electron can be captured by an atom or molecule only if the energy (electron affinity) is radiated. In some instances they are able to calculate the cross-section for electron capture of the neutral atom. Bloch and Bradbury (98) also consider the mechanism of electron capture in gases where dissociation does not occur and they explain capture by a process involving excitation of molecular vibration levels and subsequent loss by collision or resonance.

Thermochemical calculations. Born (15) and Fajans (16) have calculated the electron affinity of chlorine, bromine, and iodine atoms from a knowledge of the following quantities:

U = the grating energy of a crystal of an alkali halide (MX). It is the electrical work which must be done to dissociate one mole of the crystalline salt into a mole of gaseous alkali ions M^+ and one mole of halide ions X^-. Values of the grating energies are obtained from purely electrostatic calculations on the view that the crystal is made up of positive alkali metal ions and negative halide ions. Born and Mayer (17) have recently recalculated some of these grating energies.

I_M = the ionization potential of the alkali metal M as obtained from spectroscopic data.

S_M = the heat of sublimation of the alkali metal.

D_{X_2} = the heat of dissociation of the halide molecule X_2 into atoms X.

Q_{MX} = the heat of formation of the solid alkali halide.

E_X = the electron affinity of the halogen atom.

The following reactions permit the calculation of the electron affinity:

$$M \text{ (solid)} \rightarrow M \text{ (gas)} \qquad -S_M$$

$$M \text{ (gas)} \rightarrow M^+ \text{ (gas)} + E^-\text{(gas)} \qquad -I_M$$

$$X \text{ (gas)} + E^-\text{(gas)} \rightarrow X^- \text{ (gas)}$$

$$M^+\text{(gas)} + X^-\text{(gas)} \rightarrow MX \text{ (solid)} \qquad +U_{MX}$$

$$MX \text{ (solid)} \rightarrow M \text{ (solid)} + \tfrac{1}{2}X_2\text{(gas)}$$

An excellent discussion of this topic is given by van Arkel and de Boer (18). The latest calculations are contained in a paper by Mayer and Helmholz (19) and Mayer and Maltbie (20). They find the following values: fluorine (4.14), chlorine (3.76), bromine (3.55), iodine (3.22 e.v.). Energy is given out as the electrons attach themselves to the corresponding atoms. However, the production of doubly charged oxygen ions (O^{--}) and sulphur ions (S^{--}) requires the addition of 6.50 and 3.92 e.v., respectively. These last two ions would not be stable in the free state.

It is seen that the halogen atomic ions are stable and they may be expected in discharge tubes where dissociation of the molecules can take place. On the other hand it is of interest to note that doubly charged oxygen and sulphur atomic ions in the free state are highly unstable structures as has also been pointed out by van Arkel and de Boer (18).

The ions O^{--} and S^{--} should therefore not be found in gaseous discharges. Mayer and Maltbie also pointed out that the electron affinities (21, 22, 23) of O^- and S^- can be estimated from the ionization potentials of Ne^{++} and F, Ar^{++} and Cl by extrapolation (Moseley curves) which yields 50 and 65 k-cal., respectively. It appears then that the singly charged ions O^- and S^- are stable from an energy point of view.

Latimer (24) has shown that the entropies of solution of the halide ions are in agreement with the known electron affinities of these elements. The electron affinity of hydrogen has also been calculated from the grating energies of the alkali hydrides (25–30). The values vary between -1.0 and $+35$ k-cal. and are not to be considered so trustworthy as the value calculated by wave mechanics (Section 3).

Thermodynamic equilibrium at high temperature. The most direct determination of electron affinity has been made by Mayer (31), who measured this quantity for iodine. He studied KI and CsI at high temperature (1100° K.). These salts will dissociate into ions at a sufficiently high temperature in accordance with the reaction

The equilibrium constant (K_T) for this reaction is

$$P_{\mathrm{MI}}$$

where P_{MI} is the vapor pressure of the salt in question at the temperature T of the furnace and P_{I^-} is the pressure of the positive or negative ion at equilibrium. The vapor pressure of the salts was obtained from the data of Wartenberg and co-workers (32, 33) and the pressure of the ions was calculated from the geometry of the apparatus and the current which issued from a small hole in the furnace in a Faraday cage.

The free energy ΔF_T of the reaction can be calculated from the equilibrium constant by

$$\Delta F_T + \Delta (PV)_T = RT \ln K_T$$

where $\Delta (PV)_T$ is the change in the pressure-volume product during the process and R = the gas constant per mole. The energy change ΔE_T for the same reaction is

$$\Delta E_T = \Delta F_T - T \Delta S_T$$

where ΔS_T is the change of entropy during the process. This latter quantity is obtained by calculating the entropies of MI, M^+ and I^- from general theoretical propositions. These considerations enable Mayer to evaluate the energy changes (at 0° K.) of the dissociation of the salts into ions. Their dissociation into atoms has been studied by Sommermeyer (34). The ionization potentials of the metals are known very accurately from spectroscopy, and it is then possible to evaluate the electron affinity from three reactions:

	$I^- - 104.6$ Cal.	$CsI \rightarrow Cs^+ + I^-$	$- 94.8$ Cal.
$K + I$ · KI	$+ 76.5$ Cal.	$Cs + I \rightarrow CsI$	$+ 77.0$ Cal.
$K^+ + E^-$ · K	$+ 99.6$ Cal.	$Cs^+ + E^- \rightarrow Cs$	$+ 89.5$ Cal.
	$+ 71.5$ Cal.		$+ 71.7$ Cal.

After considering the sources and magnitudes of error involved in the method, Mayer states that the electron affinity of iodine is 72.6±2 k-cal. The agreement between this value and the value calculated from grating energies (74.2 k-cal.) is very satisfactory indeed, and one sees that the electron affinity of iodine is known with considerable accuracy.

Sutton and Mayer (35) and Glockler and Calvin (36) studied the behavior of the emission from hot tungsten filaments at high temperature in iodine vapor. Iodine molecules become dissociated at the hot filament, and some of the atoms unite with an electron at the filament surface. The current leaving the filament is thus carried partly by electrons and partly by negative iodide ions. Sutton and Mayer determined the ratio of electron to ion current by a magnetic device, and Glockler and Calvin obtained this ratio from the space-charge relations pertaining to the case. It is assumed that equilibrium between electrons, atoms and ions is attained at the high temperature surface of the filament, and the equilibrium constant of the reaction

$$\mathrm{I} + \mathrm{E}^- \rightleftharpoons \mathrm{I}^-$$

is

$$K = e^{-\Delta F/RT_s} = \frac{P_{X^-}}{P_X \cdot P_{E^-}} = \frac{Z_{X^-}}{Z_X \cdot Z_{E^-}}\,(2\pi\, m_{E^-}\, kT_s)^{-1/2}$$

where ΔF = free energy change of the process; T_s = temperature of the filament; P_a = the partial pressure of the species a; Z_a = the number of impacts of species a with unit area of the filament per second; m_{E^-} = mass of the electron; k = the gas constant per molecule; $Z_a = P_a/(2\pi m_a k T_s)^{1/2}$. The final expression for the electron affinity $(-\Delta E_0)$ is

$$-\Delta E_0 = \left(\frac{4.575}{1000}\right) T_s \,[\log F - \log P_{\mathrm{I}_2} + 2 \log T_s + 1.073] \text{ k-cal.}$$

F = the ratio of ion to electron current; P_{I_2} = the pressure of molecular iodine vapor.

Sutton and Mayer obtained a value of 72.4 k-cal. and Glockler and Calvin found 74.6 k-cal. for the electron affinity of iodine. Since these values check other methods of determination very well, it can be said that the assumptions underlying these experiments are reasonable and that the electron affinity of iodine atoms is a well-known quantity.

Glockler and Calvin (37) have also determined the electron affinity of bromine atoms using their method of space charge effects, and they obtain a value of 88 k-cal. Rogowski (99) discussed the problem of electron attachment on the basis of the mass action law.

Conductivity of flames. It is well known that flames have an appreciable conductance, and this interesting observation has been the subject of several researches. One may mention the work of Wilson (38, 39), which is of special interest in this connection for Noyes and Wilson (40) interpreted the experimental results of Wilson on a thermodynamic basis as had been done earlier by Eggert (41) and especially by Saha (42), who considered the effect of high temperature on the equilibrium of such a reaction as the ionization of a metal like sodium:

$$\text{Na (gas)} \rightarrow \text{Na}^+\text{(gas)} + \text{E}^-\text{(gas)}$$

The study of the equilibrium relations to be expected from thermodynamics led Noyes and Wilson to determine the ionization potential with very satisfactory results of some of the alkali metals, when they were introduced into flames. The flame conductivity is measured, and the flame must be calibrated by knowing the ionization potential of one of the elements of a mixture of two metals which is introduced into the flame. The same considerations and methods were employed by Rolla and Piccardi (43), who also measured the ionization potential of various elements such as the alkaline and rare earths and others (43).

An interesting extension of the method of flame conductance measurement was made by Piccardi (44), who found that this method of determining ionization potentials is directly applicable to the determination of the affinity of an atom for an electron. But the reaction

$$\text{Neutral atom} + \text{Electron} \rightarrow \text{Negative ion}$$

involves not an increase but a decrease in the flame conductivity. The ionization in the case of iodine of the iodine atom itself does not interfere, and the electron affinity of iodine atom is found to be 82,000 cal. or 3.57 e.v. The use of ethyl bromide in the flame permitted the study of the electron affinity of bromine atom, which was found by Piccardi (44) to be 86,700 cal. or 3.7 e.v.

Piccardi (45) also studied the electron affinities of stable molecules and obtained values for sulphur dioxide and selenium dioxide. The reaction taking place in the flame and producing a diminution of the conductivity is:

$$\text{Neutral molecule} + \text{Electron} \rightarrow \text{Negative Mole Ion}$$

For sulphur dioxide he finds:

$$SO_2 + E^- \rightarrow SO_2^-,\ 2.8\ \text{e.v.}$$

and for selenium dioxide:

$$SeO_2 + E^- \rightarrow SeO_2^-,\ 2.3\ \text{e.v.}$$

If the molecules investigated do not dissociate at the temperature of the flame (2000° K.), the results should be satisfactory. This method furnishes at present the only means of determining the electron affinity of molecules in a direct experiment.

Spectroscopic determination. In the case of the recombination of a positive ion and an electron it may be expected that the excess of energy is emitted as radiation. The frequency of light emitted would be the convergence frequency of the principal series of the atom, with an attendant continuous spectrum on the short-wave-length side due to the fact that the incoming electron may have various velocities relative to the positive ion. Such spectra have been observed in the case of hydrogen (46) with the Lyman and Balmer series. The same relation may be expected in the case of an atom with electron affinity, for example, neutral chlorine atom:

$$\mathrm{Cl} + \mathrm{E}^- \rightarrow \mathrm{Cl}^-,\ \Delta E = h\nu$$

This equation represents the union of a neutral chlorine atom (Cl) and an electron (E^-) resulting in the formation of a negative chlorine ion (Cl^-). Accompanying this chemical reaction is an emission of energy (ΔE = electron affinity) in the form of radiation of frequency ν. The constant h is Planck's constant. Since the incoming electron may have some kinetic energy relative to the neutral chlorine atom, a continuous spectrum is to be expected at the short-wave-length side of the frequency ν. This electron affinity spectrum was discussed by Franck (47), who so interpreted a band found by Steubing (48) in the emission spectrum of iodine vapor. The long-wave-length limit of this band has a frequency which corresponds to 2.57 e.v. which is at least of the order of magnitude of the electron affinity of iodine atom. For the electron affinity of the bromine atom Franck gives 2.93 e.v. Angerer (49) and Gerlach and Gromann (50, 51) obtained for chlorine and iodine 89,300 and 81,800 cal. for the respective electron affinities, interpreting two continuous bands at 3180 Å and 3460 Å in the way just outlined. However, Oldenberg (52) and Ludlam (53) showed that the evidence that these bands are associated with atoms is unsatisfactory, and they demonstrated that they are not electron affinity spectra as has been assumed. Franck (54) agrees with their conclusion. Oldenberg thinks that these bands may be connected with a process of recombination of positive and negative ions in the discharge tube. If these bands do not represent electron affinity spectra, it is remarkable that the energy values calculated from them fit so closely to values obtained by other methods. It appears then that the direct spectroscopic determination of electron affinities has not yet been accomplished.

Franck (54) pointed out that it should be possible to determine the electron affinity of halogens from a study of the ultraviolet absorption spectrum of gaseous alkali halides. Angerer and Müller (55) studied the long-wave-length absorption limit of thermally dissociated alkali halide vapors and calculated from their measurements values for the electron affinities of the halogens which agree quite well with other determinations. However, Lederle (56) pointed out that the long-wave-length limit of the continuous bands observed by Angerer and Müller are not sharp and that these spectra must be ascribed to the halide molecules as such and that they are not electron affinity spectra in a direct sense. He suggested that the maxima of the continuous spectra can be determined more accurately than their long-wave-length limit. He supposed that the process corresponding to the light emission of these bands amounts to a dissociation of the halide molecule into an alkali and a halogen atom, which separate with relative kinetic energy. He compared the optical energy values of this dissociation with values calculated by Born and Heisenberg (57) as obtained from ionization potentials of the metals and electron affinities of the halogens and was able to derive the following values: $E_{\mathrm{Cl}} = 90$, $E_{\mathrm{Br}} = 82$ and $E_{\mathrm{I}} = 73$ k-cal. The electron affinity of fluorine ($E_{\mathrm{F}} = 95{,}000$ cal.) was obtained by several empirical methods involving graphical comparison of electron affinity and atomic number, or maxima of continuous absorption of the halogen molecules or their heat of dissociation. However, Kuhn (58) remarked that the considerations of Lederle are unsatisfactory and the agreement of the values for electron affinities obtained with other methods is fortuitous.

It is seen then that the direct electron affinity spectrum has as yet not been observed although it should be possible to do so (59–62). It may be that the spectrum is too weak and that it occurs in a spectral region where there also appears radiation due to other processes which have greater probability, in the discharge tubes used to date. However, from the maxima of the continuous absorption bands of the alkali halides it has been possible to deduce the electron affinities of the halogens.

Another method may be suggested here which is due to Herzfeld and Wolf (63), who calculated the molar refractivity of several alkali halides. This calculation involves the electron affinities of the halogens, and, conversely, from the known refractivity of these salts the electron affinities of the anions can be calculated.

Dissociation by electron impact. The modern development of mass spectroscopy has been extended by Tate and his students (64, 65) to a study of the dissociation products obtained when molecules are dissociated into charged and neutral portions upon electron impact. Of particular importance is the knowledge obtained by these investigators of the kinetic energies of the resulting products of decomposition. Such experiments permitted Lozier (66) to obtain 2.2 e.v. for the electron affinity of the oxygen atom, and Hanson (67) estimates the electron affinity of chlorine to be about 4 e.v.

Qualitative evidence. Besides the phenomena discussed which yield quantitative results there are other indications of a qualitative nature which also show that certain atoms and molecules must have the ability to combine with electrons and form stable structures called negative ions. Warburg (68) very early noted the effect of a small amount of oxygen on the conductivity of gases, and Reichenheim (69) mentions that the anode drop in ordinary gases is 20–40 volts, while the admixture of halogens changes it to several hundred volts. He showed that phosphorus vapor has a similar effect. Franck (70) noted that the mobility of negative ions in pure argon gas is changed by addition of 1.5% of oxygen from a value of 206 cm./sec. per volt/cm. to 1.7 cm./sec. per volt/cm. He assumed that the first high value of the mobility is due to nearly free electrons; that, however, the added oxygen molecules catch these electrons; and that the resulting negative ions have the smaller mobility. The mobility of the positive ions in argon is not affected by the addition of oxygen. The rare gases when pure are especially able to keep electrons in the free state while slight impurities have a very great effect and reduce the mobility of the negative carriers very markedly. Franck (71) found that the order of the electronegative character of several gases is the following: Cl_2, H_2O, NO, O_2, H_2, N_2, rare gases. Chlorine is the most electronegative gas in this series, and the rare gases show no tendency to add an electron. The same series is obtained by Franck and Wood (72), who studied the influence upon the fluorescence of iodine and mercury vapors of these various gases, which shows that these molecules affect the emitting iodine or mercury atom in a way that depends upon their own tendency to unite with electrons.

Stark and his co-workers (73, 74) studied the effect of added gases like iodine and oxygen on the canal rays of helium, and the electronegative nature of the first of these gases was manifested by the change that they brought about in the light emission of the helium canal rays. They found only positive rays in helium and mercury, and the addition of iodine increased the number of positive particles, which was explained by assuming that the added iodine removed electrons to a sufficient extent that the chances for neutralization of the positive ions of helium were lessened, permitting them a longer existence in the beam. However, Franck (75) prefers to think that the neutralization by electrons is of only secondary importance in a canal ray and that the neutral iodine actually robs a neutral helium or mercury atom of an electron, provided that there is enough relative kinetic energy to carry out such a process.

Franck and Hertz (76) then showed that slow electrons can make elastic impacts in a gas such as helium which possesses no electron affinity whereas in oxygen such impacts are decidedly inelastic even at very low velocities.

The effect of oxygen and water vapor on the ionization current produced by alpha particles in argon shows also that oxygen and water vapor catch electrons. This phenomenon has been studied by da Silva (77). It is by no means clear in the case of diatomic molecules like Cl_2 whether the molecule itself also has an electron affinity because in many experiments it may have been possible that the molecule became dissociated and then the electron affinity of the atom will have to be taken into account in the further action of the halogen. On the basis of energy considerations, it is possible as Fajans (78) points out that, for example, halogen molecules may appear to have an electron affinity:

$$\begin{array}{lll} & X_2 \rightarrow 2X & (\mathrm{Cl}: -2.47, \mathrm{Br}: -1.96, \mathrm{I}: -1.53\ \mathrm{e.v.}) \\ X + E^- & X^- & (\mathrm{Cl}: +3.76,\ \mathrm{Br}: +3.55,\ \mathrm{I}: +3.22\ \mathrm{e.v.}) \\ X_2 + E^- \rightarrow & X + X^- & (\mathrm{Cl}: +1.29, \mathrm{Br}: +1.59, \mathrm{I}: +1.69\ \mathrm{e.v.}) \end{array}$$

The last-mentioned reaction can take place with liberation of energy as indicated by the negative sign. Halogen molecules can then remove electrons from a gas stream without forming negative mole ions. The mole ions formed in accordance with

$$X_2 + E^- \rightarrow X_2^-$$

may possibly exist, for some energy-rich molecules are well known to have reasonably long lives. However, in the case of chlorine Dechend and Hammer (79) have found Cl^- ions but no Cl_2^- ions in canal rays. Whether a given molecule will dissociate upon interaction with an electron depends upon the relative values of the heat of dissociation into its parts and their electron affinity. For example, in the case of oxygen it is more likely that a molecular ion should be stable when the heat of dissociation of the molecule and the electron affinity of the atom are considered.

Thomson (1) remarks that, of the ordinary gases, oxygen is the only one observed to furnish a negative molecular ion (97). On the other hand, Loeb (80) and Bradbury (81, 89) determine, from measurement of mobility, the coefficient of attachment of electrons to NH_3, CO, NO, HCl and Cl_2, while Bradbury and Tatel (90) studied CO_2, N_2O, SO_2, H_2S and H_2O. In many gases dissociation happens, and for example NH^- appears in ammonia gas. Again it is seen that evidence from mobility measurements of the negative carriers in gases favors the idea that electrons attach to atoms or molecules forming negatively charged bodies (94, 95). Although it might be thought that such attachment is most probable when the electron has zero velocity relative to the atom or molecule, there has also appeared in the literature the suggestion that electron attachment is more probable at some critical relative electron speed. Hey and Leipunskii (82) state that electrons of zero velocity and of a velocity corresponding to 2–4 e.v. attach themselves most readily to iodine molecules. With argon and mercury, and low-speed electrons, negative ions were not detected. At velocities near and above the ionization potentials, negative ions of argon and mercury were observed and the probability of their formation is of the order of 10^{-5}. Bradbury (91) makes the attempt to relate the electronic configuration of molecules and their possible electron affinity. Highly symmetrical molecules ($^1\Sigma$ states) do not have an electron affinity. On the other hand, molecules existing in such states as $^2\Sigma$, $^3\Sigma$ and $^2\Pi$ show a tendency to add electrons.

Electron affinity of radicals. Although thus far the formation of negatively charged molecules and atoms has been considered, it is quite clear that radicals also should possesss the ability to form negative structures by the capture of an electron. It is then possible to speak of the electron affinity of radicals such as methyl, etc. Free radicals are known to have a great affinity for electrons, and the electron affinity of triphenylmethyl, for example, has been measured by Bent (83) to be 59±5 k-cal. He found the addition of sodium to triphenylmethyl to be a reversible reaction and was able to calculate the free energy of the reaction. Further thermochemical treatment led to the above result. Bent and co-workers (84–86, 93) also determined the electron affinity of more complicated free radicals to be about 60,000 cal.

The electron affinity of the hydroxyl and cyanide radicals which are "halogen-like" has been estimated on an empirical basis by

Lederle (87). He related the heat of dissociation of halides, the energy of maximum absorption and the electron affinity and found

$$\mathrm{OH} + \mathrm{E}^- \rightarrow \mathrm{OH}^-, \Delta E = 3.8\,\text{e.v.}$$

$$\mathrm{CN} + \mathrm{E}^- \rightarrow \mathrm{CN}^-, \Delta E = 4.0\,\text{e.v.}$$

Weiss (92) used the method of a Born-Haber cycle to obtain the electron affinities of HO_2, OH and O_2:

$$\mathrm{HO_2} + \mathrm{E}^- \rightarrow \mathrm{HO_2}^-, \Delta E = 4.6\,\text{e.v.}$$

$$\mathrm{OH} + \mathrm{E}^- \rightarrow \mathrm{OH}^-, \Delta E = 3.7\,\text{e.v.}$$

$$\mathrm{O_2} + \mathrm{E}^- \rightarrow \mathrm{O_2}^-, \Delta E = 2.7\,\text{e.v.}$$

Other evidence that radicals can exist as negative ions has been obtained by Mecke (88), who showed that the carriers of the band-spectra of ionized hydrides of beryllium and magnesium probably are $(\mathrm{BeH})^-$ and $(\mathrm{MgH})^-$.

It must then be abundantly clear that, in regions where electrified particles exist, there are possible negatively charged atoms or molecules and radicals depending on the gases present in such devices as discharge tubes or ozonizers or any region of high electrical fields. Whatever chemical actions are produced in these electrical devices, their mechanism must include the possibility of the activating action of such negatively charged ions. The subject has lately been reviewed by Massey (100).

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CHAPTER XVI

MOBILITY OF IONS

Introduction. The study of the mobilities of ions in gases has centered around the question of their mass. Are the charged carriers monatomic or monomolecular, or do they cluster other neutral atoms or molecules? Some change in mass they must suffer, for they show different speeds under different conditions. The same question is of interest in the consideration of the chemical reactions which may take place in electric discharges. The subject of ion mobility will be considered here only in so far as its study throws light upon the clustering ability of charged atoms and molecules.

The mobility of gaseous ions has been of great interest to physicists, for it was hoped that the nature of the charged carriers in the gas could perhaps be elucidated by studying their motion in an electric field. Such detailed information would help also in advancing our knowledge of the general nature of electrical discharge in gases. The whole subject has been summarized from the point of view of the physicist by J. J. and G. P. Thomson, Przibram, Loeb and recently by Tyndall (1–5).

The mobility of positive ions in air at room temperature (20° C.) and 760 mm. Hg pressure is found to be 1.36 cm./sec. per volt/cm. The ions were produced by a variety of methods (alpha particles, X-rays, electrical discharges, ultra violet light, etc.). The negative ion in air under the same conditions and produced by the same agents has a mobility of 1.91 cm./sec. per volt/cm. In hydrogen the respective values are 5.78 and 7.89. In the rare gases and in nitrogen, under certain conditions the negative ion is the free electron, because some extraordinarily high values of mobility were found when the gases investigated were very pure. The presence of other gases and vapors has a great influence. Loeb (3) and Przibram (2) give values of the mobilities of the ions in many vapors which vary between 0.15 and 2.00. Erikson (6) found that the mobility of the positive ion in air decreased with age (a few tenths of a second) from 1.87 to 1.36. The negative ion in air has a mobility of 1.87 which it maintains under a wide variety of conditions. It soon became apparent that impurities have a great effect upon the mobility of the ions in all gases. Tyndall and Powell (7) in 1930 go so far as to say: "One is led to the conclusion that no significance can be attached to the values of the mobility of the positive ion so far obtained in any gas." It will appear in the sequel that certain gases, when present as impurities, can have a very pronounced effect upon the mobilities of gaseous ions, for, if the ionization potential of the impurity is lower than that of the molecules of the main body of gas or if the impurity is a so-called electronegative gas, then certain processes of exchange can take place which will have a decided influence on the mobility of the gaseous material present. It is of interest to note in detail the mechanism of mobility, the processes taking place in a gas containing ions, and to examine the theories of ionic mobilities in order to discover how far these considerations will support the idea of ion clusters, for the interpretation of chemical reactions in ionized gases must certainly rest in part on the view that such ion clusters exist in regions of gaseous discharge.

Processes in an ionized gas. Ionization and recombination. When a gas is ionized, the primary process which takes place is accepted to be

$$M \rightleftharpoons M^+ + E^-$$

M = neutral atom or molecule; M^+ = a single charged ion of molecular or atomic size; and E^- = the free electron. The reverse process which occurs later is the recombination of the charged particles, provided no other act has intervened. The momentary concentration of ions produced by any ordinary agency is of a lower order of magnitude than the concentration of neutral molecules. Consequently each ion collides many times with neutral molecules before recombination with an ion of opposite sign occurs. Or if the gas should happen to contain an impurity, then the ions will also make some impacts with these foreign molecules.

Electron exchange. If a charged ion of the gas should impinge upon a neutral molecule of an impurity having a lower ionization potential, it is conceivable that the ionization will be transferred to the molecule of the impurity. The reverse of the process is less likely to happen, because the first action is exothermic and consequently the reverse is of course endothermic. If the ionization potential of the impurity is lower than that of the majority of the gas molecules, additional energy must be supplied to cause the ionization to flow from the impurity to the atoms or molecules of the gas:

$$M^+ + I \rightarrow M + I^+ + \Delta U$$

I = neutral atom or molecule of the impurity; I^+ = ionized impurity; ΔU = energy difference = difference between the ionization potentials of the gas molecules and the impurity.

This process of electron exchange has been studied by Harnwell (8) and others, and it has been used to explain several features noticed in experiments with a mass spectrograph which otherwise would appear very strange. Tyndall and Powell (7) studied the phenomenon of electron exchange very carefully in connection with their work on ion mobility. Kallmann and Rosen (9), who have considered this problem theoretically, find that the greatest probability of exchange of charge exists when the ion and the neutral body are of nearly the same ionization potential, so that no energy need be taken away or supplied during the process. The larger the difference between the ionization potentials of the two interacting bodies, i.e., the more energy would have to be removed or supplied, the less likely it is that the process will occur. The probability of interaction can be expressed as an "effective target area of interaction" and is shown as a function of "energy transfer at capture" in Fig. 74*a*. A concrete example will illustrate this. The ionization potential of helium is 24.5 e.v., of neon 21.5 e.v. and of argon 15.4 e.v. In a mixture of helium and neon the process

$$\mathrm{He}^+ + \mathrm{Ne} \rightarrow \mathrm{He} + \mathrm{Ne}^+; \quad \Delta E = 3.0 \text{ e.v.}$$

would take place quite readily; in a mixture of helium and argon the process

$$\mathrm{He}^+ + \mathrm{A} \rightarrow \mathrm{He} + A^+; \quad \Delta E = 9.1 \text{ e.v.}$$

would take place less readily barring other considerations than the exchange of energy. The reverse processes would also occur if the respective energies are supplied from the kinetic energy of the interacting particles. Again the first process is said to be more likely than the second. All these considerations are expressed in Fig. 74*a*. Tyndall and Powell (7) point out, however, that the situation must be somewhat different when high-speed positive ions interact by electron exchange with molecules as distinct from atoms. Any excess of energy not only may now appear as kinetic energy but may also be absorbed as vibrational and rotational energy of the molecule. In the reverse process, however, the energy to be absorbed must come mostly from the kinetic energy of the system, for the vibrational and rotational portions of the energy of molecules at room temperature are small. The target area must now assume an asymmetric form as is shown in Fig. 74*b*.

Furthermore, in the case of *low-speed* ions, should they exchange electrons with atoms or molecules, the situation must be still different. It will then happen that the kinetic energy of the system is not large enough to make interaction possible, and the target area must be of a form as shown in Fig. 74*c*. This possibility is of very great importance to the study of ionic mobilities, for it leads to the view that an impurity of low ionization potential will obtain the ionization and will remain so ionized since the reverse process may be quite improbable. It is clear that impurities even of a non-polar character will play an important part in mobility experiments, and it is entirely possible that in most experiments the mobility of an impurity has been measured rather than the mobility of the gas ion in question.

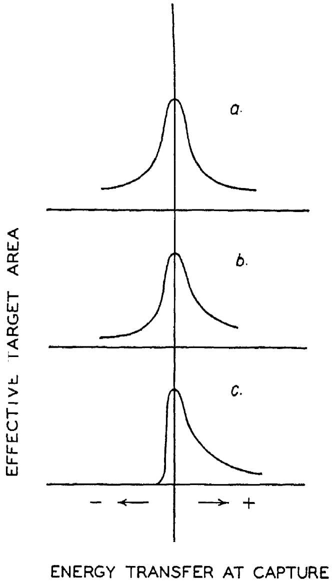

FIG. 74.—Effective target area for various interactions. Tyndall and Powell, Proc. Roy. Soc. **129**, 162 (1930).

Metastable atoms and molecules. Another process which may take place in a gas under an electrical field is the production of metastable atoms or molecules. For example, helium atoms may be brought into a metastable condition by 19.77 e.v. These metastable helium atoms, by impacts of the second kind, can ionize molecules of any impurity of lesser ionization potential. Again it is seen that an impurity may play a paramount role in determining the nature of the ions moving in a given gas. Tyndall and co-workers (27) have arranged their apparatus for mobility measurements in accordance with the best modern vacuum technique, and they find that impurities indeed play an all-important role.

Clusters. The last process to be mentioned is of greatest interest in our considerations; it is concerned with the possibility of cluster formation. The charged ion or electron may attract neutral molecules or atoms and a stable aggregate may be formed:

$$M^+ + M \rightarrow [M^+, M] \rightarrow [M,M]^+$$

This action may occur between charged particles and normal symmetrical molecules which have no dipole moment, because by induction a polarizable molecule may become a dipole and there exists then a force of attraction between the charged body and the induced dipole. If the neutral molecule already carries a permanent dipole then the resulting attractive force is larger and a more stable structure can be formed. It is to be expected that polar molecules will tend strongly towards cluster formation. Not only is it possible that polar impurities with low ionization potentials will become ionized by electron exchange, but also they have the greater tendency to be incorporated into the cluster by virtue of their inherent dipole character. It will be of great importance, therefore, to remove water vapor, ammonia, carbon dioxide, etc., from gases when they are to be used for studies of ion mobilities.

Furthermore it must be noted that the ionizing agent may produce chemical action in the gas of the type considered in this monograph. For example, in air or oxygen, oxides of nitrogen and ozone may readily be formed and the molecules of the reaction products may be of dipole nature and they will form the important ions so far as the mobility measurements are concerned, especially if they are carried out in closed vessels where impurities can accumulate. In "pure" nitrogen no chemical action due to the discharge or other ionization agent is to be expected, and indeed it has been found by the earlier investigators and again by Tyndall and Powell (7) that the negative carrier is the electron. However, the slightest trace of impurity such as may come from the metal parts and the walls of the apparatus will immediately change the nature of the negative carrier, and a slowly moving ion is the result. So there is no question but that molecules of the impurity unite with the electron to form a negative ion. This process is to be considered as the first stage of negative cluster formation. Another way of stating the case here considered is to say that the molecules of the impurity have an "electron affinity" (Chapter XV) while nitrogen molecules do not have this property. Rare gas atoms do not possess an electron affinity while most "electronegative" atoms and molecules can form stable structures with an electron, i.e., they have an affinity for electrons. One is tempted to believe that the negative carrier of mobility 1.87 found in so many gases is due to an impurity common to most gases such as water vapor and that it is perhaps not formed by the gas itself.

Aging of ions. When it is recalled that the positive ion "ages" and changes from a mobility of 1.87 to 1.36 it is clear that the simplest view of the situation is to suppose that clustering on the positive ion has taken place. Since no intermediate positive ions of mobility between 1.87 and 1.36 are found, Erikson believes that the two positive ions formed are respectively a single-molecule ion and one which has captured one molecule of the gas and thereby became a "two-molecule" ion or an ion cluster. Another alternative would be to suppose that the initial positive ion already is a larger cluster. The aged ion would then have to be considered a still larger cluster of a very special nature since no intermediate ones are found. This last view seems much more complicated, and the first hypothesis is therefore made, especially as it appears that the relative masses of a "one-molecule" ion and a "two-molecule" cluster are in the ratio of the observed mobilities.

Another observation is of interest. The peak representing the second ion (1.36) in a graph where electrometer current is plotted against mobility is much broader than the one corresponding to the initial ion. This indicates that the two-molecule ion has lesser stability and may to some extent decompose into an ion of greater mobility, i.e., the initial ion, and it also may cluster a further number of gas molecules and thereby become a slower ion. The two types of positive ions found by Erikson (6) have again been found by Tyndall and Powell (27) at low pressures in pure nitrogen, which, however, had been kept in the measuring apparatus for some time. The mobility of the initial positive ions found in the very purest nitrogen was 2.1 as compared with 1.87 of earlier investigators, and they say that it is quite possible that even these ions may not represent the true mobility of nitrogen positive ions moving through their own gas, because of possible impurities, although the nitrogen was prepared from barium azide!

Mixture of gases. The work on the mobility of ions in gaseous mixtures as summarized by Loeb (10) allows one to obtain some information as to the existence of a clustering effect of gaseous ions. From a study of Blanc's law which states that the reciprocals of the mobilities of two gases of a mixture are additive it is found that some mixtures conform to this law and others do not. In a variety of mixtures there are observed three types of effect which can be interpreted as indicating absence of clustering, labile clustering and stable clustering. The nature of the deviations from Blanc's law in various gases indicates the type of clustering to be expected. Furthermore a specific effect depending on the chemical nature of the gases is indicated. Loeb further concludes that "for pure gases the dielectric attraction of the molecules by the charged ion can account for the order of magnitude of the mobility almost as well on the small ion theory as on cluster theory." These investigations then point definitely towards clustering of molecules by gaseous ions though no quantitative results as to the size of the cluster have been obtained. Mobility experiments in mixtures have been carried out lately by Bradbury (11) in hydrogen-ammonia and nitrogen-ammonia mixtures. In pure nitrogen a positive ion of mobility 2.1 was observed, while in a mixture containing 0.01 mm. Hg of ammonia gas a larger ion of mobility 1.83 was found in addition to the normal ion in nitrogen. No negative ions were observed. In hydrogen it was noted that the addition of ammonia raised the mobility of the positive ion from 8.2 to 9.4. Bradbury found no aging in nitrogen up to 0.5 sec. whereas in air aging is found as reported previously (12). The specific effect of ammonia upon the positive ion alone can perhaps be explained by assuming the formation of the chemically stable NH_4^+ ion.

By using Loeb's method, modified to give absolute mobilities, measurements were made by Higley and Thorsen (13) in mixtures of methyl nitrite and hydrogen and methyl cyanide and hydrogen. In hydrogen the mobility of the positive ion was 7.12 and of the negative ion 10.46. In CH_3NO_2 both ions gave a value of 0.221 and in CH_3CN a value of 0.234. Of especial interest to the present discussion is the finding that deviations from Blanc's law indicate the formation of complexes. The positive ion shows the readier attachment to both methyl nitrite and methyl cyanide. These ion addition products or "clusters" are larger than the normal ion in hydrogen.

Electron attachment. The abnormal mobility of the negative carriers has been investigated in many researches. The Thomsons (1) gave the theory of this case and noted that the variation of the mobility of the negative ion with field strength and gas pressure may be due to any of the following causes: If the negative ions start initially as electrons they may attach themselves to molecules (perhaps of an impurity) and remain attached permanently. They may change back and forth between clustered ions and free electrons. They may lose their energy by inelastic collisions. If they become such slow electrons that their velocity equals the velocity of thermal agitation of the gas molecules then it will not be proportional to the field. These considerations lead to an investigation of the number of collisions which an electron will make before it will attach itself to a molecule and form a negative ion. Loeb (14, 15) and Wahlin (16) investigated these questions, and Loeb gives the following values of n, the number of collisions of an electron before attachment: N_2, H_2, CO(∞); NH_3 (10^7); CO_2, N_2O (10^6); air (10^4); O_2 (10^3); Cl_2 ($<10^3$). It is clear that nitrogen, hydrogen and carbon monoxide do not cluster readily with an electron and that oxygen and chlorine will form permanent clusters much more readily. These latter two gases are "electronegative," i.e., they possess an electron affinity (Chapter XV.)

It is further of interest to note that Loeb and Bradbury (17) come to the conclusion that ions of ages from 0.5 to 2.0 sec. show a considerable range of mobilities. This is not necessarily the case for the normal ions studied over shorter time intervals. Ions consist of one or two molecular addition products of probably dipole molecules which attach themselves to the original carrier. This mode of attachment will depend upon the nature of the molecule and the kind of charge on the ion. In other words, clustering takes place. This consideration will also furnish a basis for an explanation of the difference in mobility found between positive and negative ions. It is supposed that the chemical forces acting between ion and dipole molecule will be different depending upon the sign of the charge and upon the detailed structure of the molecule. Large molecules like alcohols which owe their dipole character primarily to the hydroxyl group may cluster quite differently with a positive ion from the way in which they cluster with a negative one (4).

Loeb (18) measured the mobilities of sodium ions from a Kunsman source in hydrogen and nitrogen gas at time intervals of 10^{-5} to 10^{-1} sec. The results indicate three classes of ions in hydrogen and probably also in nitrogen. In hydrogen a fast ion of mobility 17.5 was found which is presumably the sodium ion (Na^+) which exists under the conditions of the experiment up to 10^{-4} sec. It then changes abruptly to an ion of mobility 13.5, and after about 10^{-3} sec. it becomes the normal or usual ion in hydrogen of mobility 8.4. The intermediate ion is probably a cluster with a single molecule (water vapor). The final ion grows out of the intermediate one by further clustering. In nitrogen the initial ion up to 5×10^{-3} sec. has a mobility of 3.75, then changes to an ion of mobility 3.00 and after about 10^{-2} sec. it becomes the usual ion of mobility 1.6. Again clustering is the obvious explanation for this mode of behavior. Other investigators (19–23) carried on mobility studies.

Very pure gases. Some of the modern investigators have made the most strenuous attempts to work with pure gases in order to determine the nature of the gaseous ions from mobility experiments. Bradbury (24) studied air ions which have an age of 4×10^{-2} sec. They have mobilities of 2.2 and 1.6 for the positive and negative ion. Oxygen shows different behavior depending upon its method of preparation ($KClO_3$ or $KMnO_4$), indicating that different impurities are of importance. Nitrogen and hydrogen give no negative ions when extremely pure. The negative carriers are electrons. The positive nitrogen ions move with mobility 2.1, and the positive hydrogen ions have a mobility of 8.2 and 13.1. Helium gave no negative ions and a positive ion of mobility 17. It is noticeable that greater purity of gas tends to procure higher mobility values, showing that less clustering has taken place in the highly purified gases as compared to the impure gases used by earlier investigators or in different methods of measurement. The great effect of impurities on the mobilities of ions is shown most strikingly in spectroscopically pure helium. Whereas the mobility of the positive ion in "pure helium" has been determined to be about 6, Tyndall and Powell (7) obtained the very high value of 17 in their first trials. From these experiments it is obvious that impurities present in very small concentration (1 in 10^6) have a most profound effect on the mobilities of the gaseous ions. In a further set of extremely careful measurements, Tyndall and Powell (25) found that the mobility of positive helium ions in helium gas at 760 mm. Hg pressure and 20° C. is 21.4 cm./sec. per volt/cm. It is most interesting to note that this value for the mobility of helium ions in helium is very close to the theoretical value 26 obtained from Langevin's theory by Hassé and Cook (26). It appears then that helium positive ions do not cluster helium atoms. This is to be expected because the helium atom is a very symmetrical structure of no inherent dipole moment. But the older values of the mobility of gaseous ions in helium of about 6 can now be best explained by assuming that the initial ion either is an impurity, or, if the center is really a helium ion, that it has clustered molecules of the impurity which must be of dipole nature. Such indirect evidence speaks for the existence of clustering by ions.

Tyndall and Powell (27) measured the mobility of alkali ions (Na, K, Rb and Cs) in the rare gases argon, neon and helium, and Powell and Brata (28) completed the series by studying lithium ions in the same gases and extended the work to the gases krypton and xenon and also to hydrogen and nitrogen. The alkali ions show mobilities in the rare gases that indicate single atomic ions and no clustering is observed in the pure gases. Sodium ions in hydrogen show a mobility of 13.2, and under changed conditions where the presence of water vapor may be suspected they show the existence of another ion of mobility 11.2 which is ascribed to a cluster ($Na^+ \cdot H_2O$). Since the mobility of the alkali ions is found to be independent of the mass for all the alkali ions studied in hydrogen, the addition of a water molecule to a sodium ion must be effective in reducing the mobility to 11.2 by affecting the size of the ion rather than its mass.

It is found that the alkali ions show different mobilities in nitrogen depending on their mass. Hence it will be more easily possible to follow cluster formation of the alkali ions in nitrogen. Powell and Brata (28) find indeed indications of clustered ions in nitrogen at the higher pressures used. The first clustered ion which appeared had a mobility of 2.66 as compared to 3.04 for sodium ion in pure nitrogen. From the theoretical relation connecting mobility and mass mentioned below, it is possible to calculate that the mass of the ion would be 41, which would make the mass of the clustered molecule 18 since sodium ion has a mass of 23 on the ordinary atomic-weight scale. The polar impurities likely to be present in the apparatus containing a Kunsman source of sodium ions and nitrogen gas are the ever-present water vapor and possibly ammonia. The hydrogen may have come from the Kunsman source since it is prepared by reduction in hydrogen and the source itself is known to be a catalyst. However, in this case it seems more likely that water vapor was absent because the same sodium source in hydrogen showed no clustered ions while in nitrogen they could easily be found. They appear to be ammonia molecules attached to sodium ions:

$$Na^+ \cdot NH_3$$

And, most important for our consideration, it was found by Powell and Brata that at higher pressures a second and a third molecule of ammonia could be attached to the original cluster:

$$Na^+ \cdot 2NH_3 \quad \text{and} \quad Na^+ \cdot 3NH_3$$

The ion cluster $Na^+ \cdot 2NH_3$ of mass 57 was found to have the mobility of an alkali-like ion of the same mass. With the apparatus used in the studies just reported, Powell and Brata obtained further results which tend to show that water molecules attach themselves with greater ease to the lighter alkali atoms, and the maximum number of water molecules which can attach themselves to any alkali atom decreases with the increasing atomic weight of the alkali metal.

Loeb (29) summarizes his extensive work on ionic mobilities as follows: "The normal gas ion consists of a single charge either positive or negative to which one or two neutral molecules cluster. The clustered molecules are united firmly to the ion by chemical forces of the same nature as produce such structures as

$$[NH_3 \cdot H]^+ \text{ or } [Cu^+(CN)_2{}^{--}]$$

An initial ion may change with age depending on the amount and kind of impurity contained in the gas in which it moves. The charged nucleus may be altered by the process of electron exchange. Langevin's theory appears still fairly satisfactory."

Theory of ionic mobility. The most satisfactory theory of the motion of ions through a gas is due to Langevin (30), who treats the problem as one of diffusion. The ion is defined by its charge (e) and radius (a), and the molecule is thought of as a conducting sphere. At a distance r the two bodies will attract one another, owing to induction, with a force

$$\begin{gathered} e^2a^3(2r^2 - a^2) \\ r^3(r^2 - a^2)^2 \end{gathered}$$

Assuming that $\quad a$, the attractive force is given by

$$2e^2a^3$$

If the dielectric constant of the gas is K and N represents the number of molecules per unit volume, the force becomes

$$\begin{gathered} (K - 1)e^2 \\ 2\pi N r^5 \end{gathered}$$

With this attractive force operating between the ion and surrounding molecules Langevin obtained for the ionic mobility k:

$$k = \sqrt{d(K - 1)}\ \Bigl(\quad M)$$

The quantity A is a function of λ, which is given by

$$\lambda^2 = (K - 1)e^2$$

The main problem of the complicated theoretical calculations is the evaluation of the factor A for the various gases. The quantity A depends upon the relative importance of the elastic collisions and the attractive forces. For close collisions or large values of $(K - 1)$ the value of A approaches 0.505. The following notation should be kept in mind:

k = ionic mobility in cm./sec. per volt/cm.; T = absolute temperature; σ = distance of closest approach at a collision between ion and molecule; p = gas pressure; e = ion charge; d = gas density; R = Boltzmann constant per mole of gas; m = mass of gas molecule; M = mass of gaseous ion; K = dielectric constant of gas; $A = F(\lambda) = F(\sigma, p, K)$.

The whole theoretical topic of mobility calculations has been reviewed lately by Hassé (31) on the basis of modern kinetic-theory considerations. The most serious and arbitrary assumption made is in connection with the radii of colliding ion and molecule. It is assumed that the distance of closest approach of ion and molecule in a collision is the same as for two neutral molecules. For singly charged monomolecular ions, the mobility equation becomes

$$k = A\left(\frac{d}{2}(K-1)\right)^{-\frac{1}{2}}$$

Hassé calculated the mobilities of the ions of several common gases by means of this equation. The calculated values refer to monomolecular ions in the pure gases without clustering taking place. They are higher than the ones obtained in ordinary experiments, but in *pure* gases the calculated values are more nearly approached. These theoretical mobilities represent maximum values for the monomolecular ions, and there is of course no difference in mobility between the positive and the negative ion since they are assumed to have the same mass. The smaller experimental mobilities of these gases are explained on the cluster theory. Hassé gives the condition for clustering: the potential energy of the molecule in contact with the ion must be greater than the average kinetic energy of their relative motion:

$$\frac{(K-1)e^2}{8\pi N\sigma^4}\bigg/\frac{3}{2}RT = \frac{2}{3\lambda^2}$$

The ratio $2/(3\lambda^2)$ may be called the clustering coefficient. If $\lambda < 0.8165$ the coefficient will be greater than unity and clustering can take place. This is the case for all the common gases given in Table 25. Hassé following Langevin assumes that the positive ion of radius S will surround itself with the maximum number of similar spherical molecules of equal radius (S). Purely geometrical considerations give thus a cluster of 13 molecules. The mass of the clustered ion becomes

$$M = 13m$$

and the distance of closest approach at collision is nearly

$$\sigma = 4S$$

TABLE 25

Ionic Mobilities (cm./sec. per volt/cm.) at 15° C. and 760 mm. in the Same Gas

H. R. Hassé, Phil. Mag. [7] 1, 139 (1926)

Gas	$(K-1) \times 10^6$	Density	Monomolecular ions calculated		Clustered ions					
					Positive ions			Negative ions		
					Calculated		Experimental	Calculated		Experimental
			A	*k*	*A*	*k*	*k*	*A*	*k*	*k*
Air	543	1.2260	0.590	3.41	0.288	1.37	1.40	0.460	2.04	1.78
A	529	1.6880	.590	2.95	.297	1.23	1.37	.469	1.79	
He	66	0.1689	.590	26.6	.290	10.80	21.4*	.461	16.1	
H_2	250	0.0852	.588	19.0	.358	8.45	10.3*	.527	13.0	
O_2	491	1.3550	.590	3.38	.293	1.40	1.33	.465	2.07	1.82
CO	656	1.1850	.590	3.16	.309	1.37	1.10	.482	1.98	1.14
CO_2	898	1.8750	.585	2.12	.259	0.78	0.82	.411	1.14	1.01
NH_3	7540	0.7306	.567	1.15	.568	0.84	0.74	.588		
SO_2	8760	2.7740	.578	0.545	.478	0.33	0.44	.584		

* Latest values in spectroscopically pure gases.

The negative ion cluster is thought to be built up from an initial pair of molecules with the electron between them and a further addition of five clustering molecules, placed in the plane of symmetry of the initial pair. This gives

$$M = 7m$$

and the radius of this aggregate can be calculated by the method of Rankine (32). The clustering molecules are assumed to be molecules of the gas. On the basis of these speculations Hassé calculated the mobilities of positive and negative ion clusters (Table 25). Most of the values of λ used for the calculations of A are greater than 0.816, and no further clustering should take place.

The effect of water vapor or any other polar molecule on the mobilities of the ions has been mentioned above, and must also be considered in these theoretical calculations. Hassé assumes that a water molecule can attach to the charged ion, forming a cluster. If the radius of the water molecule is taken to be 2.24×10^{-8} cm. he finds that the mobility of the positive air ion is reduced from 1.37 to 1.15 and the mobility of the negative ion from 1.99 to 1.68. In hydrogen similarly the cluster mobility values are 4.85 and 7.37 which check better with experiment. But such improved agreement is not found in every case.

However, it must not be forgotten that the theoretical calculations made so far have not taken into account the phenomenon of electron exchange, which has a very important bearing on the questions of mobility and clustering. Hassé and Cook (26) attempt to take this effect into consideration by modifying the earlier calculations of mobilities on Langevin's theory. Some of the elastic collisions are assumed to be accompanied by an exchange of electric charge. The general effect is to reduce the mobilities of the monomolecular ions. It is to be noted that this reduction in mobility takes place in pure helium and is not due to the presence of impurities. This reduction of mobility is calculated to be 26.3, 21.0 and 17.4 for positive helium ions when the fraction of collisions resulting in electron transfer is 0, 50 and 100%, respectively. It is to be recalled that the highest value of the mobility of positive ions in helium determined experimentally is 21.4, obtained by Tyndall and Powell (25). The important question arises whether the general tendency for experimental values of mobilities to be low is to be accounted for by electron exchange or by clustering. It is clear that both effects exist. It should be recalled that sodium ions do show low mobilities due to clustering, while on account of the low ionization potential of sodium electron exchange is not possible.

The theoretical problem of the motion of a helium ion in helium gas has been attacked on the basis of modern wave mechanics by Massey and Mohr (33), and they calculate a mobility of 12 cm./sec. per volt/cm. The value 24 can be obtained by calculation if it is assumed that the interaction potentials between ion and atom become small rapidly with internuclear distance as compared with the polarization interaction.

The evidence from mobility studies of ions presented here is definitely in favor of the idea that gaseous ions form clusters of some kind. The whole process of interaction of ion and molecule is very complex indeed, and nothing very definite can be said as to the actual size of ion clusters. However, the principal idea is certainly sound, and it is permissible to use the notion of "ion clusters" in other considerations wherever this idea may be helpful as, for example, in the problem of chemical reactions in an ionized gas.

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CHAPTER XVII

IONS PRODUCED FROM MOLECULES IN ELECTRICAL DISCHARGES

Introduction. It is of greatest interest to know the types of ions which occur in electrical discharges because these charged particles may enter into the various interactions from which the chemical products are formed. The mass spectrograph (1, 2, 29) has been used extensively in investigating gaseous ions. Molecules can undergo the following reactions in electrical discharge:

1. They can lose one or more electrons, becoming molecular ions with the same mass as the original molecule with one or two positive charges. It is not exact to say that a positive ion has the same mass as the parent molecule from which it originates because the expelled electron, of course, has "mass," but the difference cannot be found in the ordinary mass spectrograph. However, these instruments can be made to determine the mass of charged particles with very high accuracy (6). The formation of molecular ions can be represented by the equation

The second reaction corresponds to the removal of two electrons in one act. It is conceivable that even three or four electrons may be removed from one molecule, but such cases have not been reported although mercury *atoms* (48) and krypton *atoms* (76) have been produced with one to five positive charges, and rubidium with one to four, xenon with one to six and cesium with one to seven (76). It appears that a molecule is more easily dissociated than charged positively to a high value, by electrons which have the requisite energy. In general, doubly charged molecules occur in greater number if an electronegative gas (O_2,Cl_2) is present in the discharge tube (61) at the same time. The extra electron can be caught more readily by the electronegative molecules mixed with the gas, thus preventing recombination:

$$M \overline{\leftarrow}$$

2. The second action which molecules suffer in a discharge region is their dissociation into atoms or into radicals of lesser weight. The

possibility of various types of dissociation is large for a complex molecule. It seems that all the radicals conceivable on valence theory can be found in electrical discharge. A clear case studied extensively may serve as example:

$$
\begin{aligned}
CH_4 \rightarrow\ & CH_4^+ + E^- \\
& CH_3^+ + E^- + H \\
& CH_2^+ + E^- + 2H \\
& CH^+ \ \ + E^- + 3H \\
& C^+ \quad + E^- + 4H
\end{aligned}
$$

These equations show the formation of various radicals which can be derived from methane by stripping hydrogen atoms from the molecule. A more complex molecule will, of course, be disintegrated into other parts. The dissociation of a molecule into small fragments can take place in a primary collision with the impacting electron, as has been shown, at least for diatomic molecules such as nitrogen, carbon monoxide and hydrogen by Tate, Lozier and others (75, 67). The impacting electron must at least have enough energy to dissociate the molecule and ionize one of the fragments. Any further amount of kinetic energy available appears in the relative motion of the resulting atoms and ions. The form of discharge has an effect on the type of dissociation which will take place in a given case. For example, Hogness and Kvalnes (39) obtained only CH_4^+ and CH_3^+ from methane when they avoided thermal decomposition by the filament. The applied voltage which gave the impacting electrons their energy is not stated, but it must have been only slightly greater than 14.5 e.v., which is the ionization potential of methane. Under these conditions they found no smaller ions such as CH_2^+, CH^+, C^+ and H^+. However, Eisenhut and Conrad (60) obtained all these ions in electric discharge. They did not state the voltage applied to their glow discharge, but it must have been several hundred volts. This indicated that fast electrons can dissociate the molecule into various radicals depending on their energy. Hogness and Kvalnes (39) also showed that the CH_3^+ ion is formed in a primary act and does not arise from a secondary process due to CH_4^+ ion. The evidence in general is very strong that molecules can dissociate into fragments by direct collision with fast electrons.

3. Molecules, however, not only *break down* into smaller fragments in electric discharge; they also *build up* into structures of greater weight as already indicated by the chemical evidence! For example, Eisenhut and Conrad (60) found, in methane gas, ions of weights

greater than 16, which is the molecular weight of methane. They obtained ions which have two carbon atoms " $C_2H_x{}^+$ " (where x = number of hydrogen atoms attached to the carbon molecule C_2). The number x may vary from 1 to 6, although the highest number actually encountered in their mass spectrograph was only four. These larger complexes can be formed only by a process of " building up " from the initial methane and/or its decomposition products. Again it appeared that all conceivable combinations can be formed. But not only " two-carbon " radicals are produced from methane but structures containing " C_3 " and " C_4 " groups are found because ions of the type $C_3{}^+$, C_3H^+, $C_3H_2{}^+$, $C_3H_3{}^+$ and $C_4{}^+$, C_4H^+ appeared in the mass spectrograph when methane was placed in the apparatus and a luminous discharge passed through it. It is clear then that a general building-up process goes on in a discharge, the extent of this action depending upon the gas and upon the electrical conditions. This process is of greatest interest to the whole topic considered in this monograph and is of fundamental importance. The possibilities for a complex molecule are really enormous, as can be seen when it is recalled (Chapter VII) that methane yields liquid hydrocarbons of high molecular weight, manyfold greater than its own mass. The evidence here presented based on the findings in a mass spectrograph indicates only the beginnings of this building-up process. Continued action of electric discharge will produce larger and larger molecules by successive addition with elimination of hydrogen until such large molecules are produced that they are liquids or solids which by condensation are partially removed from further action by the discharge. The detailed considerations of this process are mentioned in Chapter VII. Here the evidence of mass spectroscopy is presented. It should be pointed out that the experiments carried out in a mass spectrograph are always performed at very low pressure (0.1–0.0001 mm. Hg), by sheer necessity, for the mean free path of the ions studied must be large in order to obtain unambiguous results. On the other hand, chemical investigations in electrical discharge are more likely to be carried out at larger pressures in order to obtain more of the product of the electrical action. This situation must be recalled when it is attempted to compare the results of chemical activation in electrical discharge with the evidence presented here as obtained at low pressure in a mass spectrograph. The clusters formed at higher pressures may be different from the ones found at low pressures. However, it is clear that the mass spectrograph gives definite evidence of a building-up process occurring in electrical discharge even at low pressures.

4. Another reaction possible in electric discharge is the attachment

of electrons to atoms, radicals and molecules with the consequent formation of negative ions. Whenever such an attachment is possible it is said that the original structure has an electron affinity (Chapter XV). A great deal of information is at hand regarding this topic, and for many atoms and radicals one can calculate and predict its magnitude. Whenever the general valence considerations and thermochemical information indicate that a given structure should be able to exist as a negatively charged ion, it is usually found in the mass spectrograph. For example, H^-, I^-, Cl^-, O^-, OH^- are negatively charged ions which occur in a mass spectrograph. However, many other atoms can attach an electron and form a negative ion: He^-. CH_2^-, CH^-, C_4^-, C_3^-, C_2^-, C^-, N^-, K^-. The attachment of an electron to a helium atom is unexpected, at least on the Bohr theory and on the basis of the behavior of helium gas in ion mobility experiments (Chapter XVI). However, according to wave mechanics all atoms and molecules have an attractive "van der Waals field" decreasing as the inverse sixth power of distance, and it may be suspected that all types of negatively charged ions are possible. Even on classical theory one would expect a polarizable molecule to have an interaction with a charged body like an electron, and on such views the findings of mass spectroscopy can be understood and there need be no conflict with our ordinary ideas of chemical valence. Molecular negative ions such as H_2^-, H_2O^-, N_2^-, O_2^-, Cl_2^-, I_2^-, I_3^-, $H_2O_2^-$ have been reported. It appears that no gaseous ions with a double negative charge have been found, which is very interesting as one would expect that they would be formed with greater difficulty since in their formation it is necessary to add one more electron to an already negatively charged structure. However, they should be possible especially with larger molecules where the two negative charges could reside on different portions of the molecule.

5. Ions in discharge tubes may be in excited states, and in this sense they may be energy-rich and will then emit light which may be photochemically active. This situation will not affect their discovery in a mass spectrograph, for they will have returned to normal states before they have reached the detecting device, and the deflection of an excited ion in a magnetic and electric field will not be different from the behavior of a normal ion of the same charge and mass. From the point of view of the possible chemical reactions in a discharge, however, these excited species and their radiations are important, for it must be recognized that they may react differently when in the excited state and the possibility of photochemical action must be kept in mind.

It has already been pointed out that ions may occur with double positive charges, and it is found that such ions can catch an electron and then become of single charge and as such they are identified in the mass spectrograph. This change in charge has been studied frequently, and of course the further neutralization with the formation of neutral particles goes on in every discharge which is noted in the mass spectrograph by the formation of the "neutral spot," due to high-speed neutral atoms, etc., which have been accelerated as charged bodies but have lost their charge but not their speed by subsequent neutralization.

The physical study of "canal rays" has been brought to a remarkable perfection, and a great deal of valuable information has been obtained and is contained in the literature cited. The ionization potentials of molecules have been determined; the mass of the resulting ions has been measured; their kinetic energies have been found. In spite of all this progress, however, it must be said that much more knowledge of the kind mentioned must be accumulated before a great deal is known of the electric discharge and before a complete mechanism of its chemical action can be announced.

However, it is known that: "Molecules will lose one or two electrons and form single and double charged ions, they will dissociate into smaller fragments by electron impact, they and their dissociation products will undergo a process of 'building-up' to structures of higher molecular weight. Molecules and their dissociation and aggregation products will add electrons and they will form negatively charged ions."

It is well known, of course, that the mass spectrograph has been used to find the isotopes of the elements by Aston (6) and others. These experiments are not discussed, since they do not bear directly on the subject matter of this monograph. The ions of water and air are likely to be present in any discharge tube. They originate from gases on the wall. The results of mass spectroscopy are given in the following pages. The lowest potentials (in electron volts) at which a given species of ions appears are mentioned in parentheses. At times a process may be of such a nature that the products of decomposition separate with considerable kinetic energy (K. E.). (Ref. 58, 67, 88.)

Results of mass spectroscopy:

(1) *Hydrogen:* H_2^+ (15.9); H^+ (17.9); H_3^+ (17.9); H^+ + K.E. (26 ± 1); H_4^+; $2H^+$ (31.4); $2H^+$ + K.E. (48 ± 2); H_2^-; H^-. (Refs. 1, 3, 5, 7, 10–16, 18, 24, 25, 28, 29, 32–34, 37, 58, 62, 64–67, 73, 84, 89, 91.)

(1.2) *Hydrogen and rare gases:* H_2^+ (15.9); He^+ (24.5); HeH^+; H^+; HeH_2^+; NeH^+; AH^+; HeD^+. (Refs. 1, 15, 77, 78, 85, 89.)

(1.6) *Methane:* CH_4^+ (13.1); $CH_3^+ + H$ (14.4); $CH_2^+ + 2H$ (15.7); $CH^+ + 3H$ (23.3); $C^+ + 4H$ (26.7); H_3^+ (25.3); $H_2^+ + C + H$ (27.9); $C + 3H + H^+$ (29.4); $CH_2^+ + H + H$ (22.9); $CH + H_2 + H^+$ (22.7); CH_x^+ ($x = 0$ to 4); $C_2H_x^+$ ($x = 0$ to 4); $C_3H_x^+$ ($x = 0$ to 3); $C_4H_x^{++}$ ($x = 0, 1$); CH_x^{++} ($x = 0, 1, 3$); $C_2H_x^{++}$ ($x = 0$ to 4); doubly charged ions strong in mixtures with oxygen and chlorine; C^-; CH_2^-; C_2^-; C_4^-; CH^-; H^-. (Refs. 1, 29, 39, 58, 60, 61, 67, 89, 93.)

(1.6) *Ethane:* H^+; CH_x^+ ($x = 0$ to 4); $C_2H_x^+$ ($x = 0$ to 6); $C_3H_x^+$ ($x = 0$ to 6); C_2^-. (Refs. 1, 60.)

(1.6) *Propane:* CH_3^+; $C_2H_x^+$ ($x = 3$ to 5); $C_3H_x^+$ ($x = 1$ to 8); see also methane and ethane. (Refs. 57, 67.)

(1.6) *Butane:* CH_3^+; $C_2H_x^+$ ($x = 3, 4, 5$); $C_3H_x^+$ ($x = 3$ to 7); $C_4H_x^+$ ($x = 1$ to 10). (Refs. 57, 67.)

(1.6) *Hexane:* CH_x^+ ($x = 0$ to 4); $C_2H_x^+$ ($x = 0$ to 6); $C_3H_x^+$ ($x = 0$ to 8); $C_4H_x^+$ ($x = 0$ to 9); $C_5H_x^+$ ($x = 0$ to 10); $C_6H_x^+$ ($x = 0, 1, 3, 4, 5, 6, 8$); C^-; CH^-; CH_2^-; CH_3^-; C_2^-; C_3^-; C_4^-. (Refs. 1, 87.)

(1.6) *Ethylene:* $C_2H_4^+$ (10.8); $C_2H_3^+$ (14.1); $C_2H_2^+$ (13.4); C_2H^+ (19.2); C_2^+ (26.4); CH_4^+; CH_3^+; CH_2^+ (19.2); CH_2^+ and K.E. (40.0); CH^+ (22.9); C^+ (24.6); H_2^+ (22.4); H^+ (26.2); H^+ (28.2); $C_2H_4^{++}$; $C_2H_3^{++}$ (36.0); $C_3H_x^+$ ($x = 0$ to 6); C_4^+; C_2^-. (Refs. 1, 60, 96.)

(1.6) *Acetylene:* $C_2H_2^+$ (11.2); C_2H^+ (17.8); C_2^+ (23.8); CH^+ (22.2); C^+ (24.5); H^+ (21.7); H^+ (25.6); CH_x^+ ($x = 0$ to 4); $C_2H_x^+$ ($x = 0$ to 5); $C_3H_x^+$ ($x = 0$ to 2); $C_4H_x^+$ ($x = 0$ to 2); $C_2H_2^-$; C_2^-. (Refs. 1, 60, 76, 86, 90, 96.)

(1.6) *Benzene:* $C_6H_6^+$ (9.8); $C_6H_5^+$ (14.5); $C_6H_4^+$ (15.0); $C_6H_3^+$ (21.9); $C_6H_2^+$ (23.9); C_6H^+ (33.7); C_6^+ (41.9); $C_5H_3^+$ (16.8); $C_5H_2^+$ (19.1); C_5H^+ (27.4); C_5^+ (44.0); $C_4H_4^+$ (15.5); $C_4H_3^+$ (18.5); $C_4H_2^+$ (18.3); C_4H^+ (27.6); C_4^+ (40.4); $C_3H_3^+$ (16.1); $C_3H_2^+$ (23.0); C_3H^+ (27.4); C_3^+ (45.0); $C_2H_4^+$; $C_2H_3^+$ (21.1); $C_2H_2^+$ (17.9); C_2H^+ (27.1); C_2^+; CH_3^+; CH_2^+; CH^+; C^+; H_2^+; H^+; $C_6H_6^{++}$ (27.0); $C_6H_5^{++}$ (30.4); $C_6H_3^{++}$ (39.8); C_6H^{++} (>39.0); $C_3H_3^+$ + K.E. (>39.0); $C_3H_2^+$ (>39.0); C_3H^+ + K.E. (>39.0); $C_2H_3^+$ (>39.0); $C_2H_2^+$ + K.E. (>39.0); C_2H^+ + K.E. (>39.0); CH_3^+ + K.E. (29.3); CH_2^+ + K.E.; CH^+ + K.E.; C^+ + K.E. (Refs. 1, 70, 71, 87, 96.)

(1.6) *Cyclohexane:* CH_x^+ ($x = 0$ to 4); $C_2H_x^+$ ($x = 0$ to 6); $C_3H_x^+$ (0 to 8); $C_4H_x^+$, $C_5H_x^+$ and $C_6H_x^+$ ($x = 0$ to 10). (Ref. 87.)

(1.6) *Octane:* CH_x^+ ($x = 1, 2, 3$); $C_2H_x^+$ ($x = 1$ to 5); $C_3H_x^+$ ($x = 1$ to 8); $C_4H_x^+$ ($x = 1$ to 9); $C_5H_x^+$ ($x = 10, 11$); $C_6H_x^+$ ($x = 6, 11, 12$); $C_7H_x^+$ ($x = 13$ to 16); $C_8H_x^+$ ($x = 16$ to 18). (Ref. 83.)

(1.6.7) *Hydrogen cyanide.* HCN^+ (13.7); $CN^+ + H$ (20.1); $NH^+ + C$ (24.9); $N^+ + H + C$ (25.6); $CH^+ + N$ (21.8); $C^+ + N + H$ (23.8); HCN^{++} (40.0). (Ref. 96.)

(1.6.8) *Methane and water vapor:* CH_4^+ (14.5); H_2O^+ (13.0); CH_x^+ ($x = 0$ to 4); $C_2H_x^+$ ($x = 0$ to 4); $C_3H_x^+$ ($x = 0$ to 3); O^+; O_2^+; OH^+; H_3O^+; H_2O^+; $H_2O_2^+$; C_2O^+; CO_2^+; CO^{++}; CO^+. (Ref. 60.)

(1.6.8) *Methane and oxygen:* CH_4^+ (14.5), etc.; O_2^+ (12.5), etc.; CH_x^+ ($x = 0$ to 4); H_3O^+; H_2O^+; OH^+; CO_2^+; CO^+; C_2O^+. (Ref. 60.)

(1.6.17) *Methyl chloride:* CH_3Cl^+ (11.0); $CH_3^+ + Cl$ (14.7); $CH_3 + Cl^+$ (26.0); CCl^+; CH_2^+; HCl^+; CH^+; C^+; H^+. (Ref. 90.)

(1.7) *Ammonia:* NH_4^+; NH_3^+ (11.2); NH_2^+ (12.0); NH^+ (11.2); H^+; N^+. (Refs. 1, 38, 54, 58, 67, 89.)

(1.8) *Hydrogen and oxygen*: H_2^+(15.9); H^+; O_2^+ (12.5); O^+; O^-; OH^-; $H_2O_2^-$; HO_2^-; H_2O^+. (Ref. 4.)

(1.8) *Water:* H_2O^+ (13.0); H_3O^+; OH^+ (17.3); H_2^+; $H^+ + OH$ (19.2); $H_2 + O^+$ (18.8); O_2^+; H_2O^-; OH^-; $H_2O^- \rightarrow OH + H^-$ (6.6); $H_2O \rightarrow H_2^+ + O^-$ (34). (Refs. 1, 31, 58, 66, 67, 72, 81, 84, 89.)

(1.16) *Hydrogen sulphide:* H_2S^+ (10.4); HS^+ (16.9); S^+ (15.8). (Refs. 38, 50, 58, 67.)

(1.17) *Hydrogen chloride:* HCl^+ (12.9); $H_2Cl_2^+$; HCl^{++} (35.7); H^+ (18.6 and 28.4); Cl^+ (17.2 and 21.2); Cl^{++} (45.7); Cl^{+++} (160); Cl^-(1.6); Cl_2^+. (Refs. 21, 23, 27, 67, 72, 94, 95.)

(2) *Helium:* He^+ (24.5); He^{++} (76.5) strong in presence of chlorine; He_2^+; He^- (?). (Refs. 1, 2, 14, 29, 61.)

(6.7) *Cyanogen:* $C_2N_2^+$ (14.1); $CN^+ + CN$ (21.3); $C_2^+ + N_2$ (18.6); $C_2N^+ + N$ (19.8); $C^+ + CN + N$ (22.5). (Refs. 29, 49, 58, 67, 86, 90, 96.)

(6.8) *Carbon monoxide:* CO^+ (14.1); $C^+ + O$ (20.5); $C + O^+$ (24.0); $C^+ + O^-$ (22.2); $C^+ + O^+$ (34.7); CO^{++} (43.0); $C + O^{++}$ (45.5); $C + O^{++}$ (58.5); CO^-; $CO^- \rightarrow C + O^-$ (9.5); $CO^+ \rightarrow C^+ + O$ (7.1); $CO^+ \rightarrow C + O^+$ (9.4); $CO^{++} \rightarrow C^+ + O^+$ (−17.3); $CO^{++} \rightarrow C^{++} + O$ (2.5); $CO^{++} \rightarrow C + O^{++}$ (15.5). (Refs. 29, 40, 44, 45, 52, 58, 67, 68, 74–76, 79, 80, 84.)

(6.8) *Carbon dioxide*: CO_2^+ (14.4); $CO + O^+$ (19.6); $CO^+ + O$ (20.4); $C^+ + O + O$ (28.3); $CO_2 + CO_2^+ \rightarrow 2CO + O_2^+$ (20.0); $O^+ + CO^+$ (33.3); $O^+ + O^+ + C$ (42.7); $O^+ + C^+ + O$ (40.5);

$C^{++} + O + O$ (51.2); $O^{++} + CO$ (54.2); $O^{++} + C + O$ (64.2); $CO^{++} + O$ (49.7); $CO_2^+ \rightarrow CO^+ + O$ (5.8); $CO_2^+ \rightarrow CO + O^+$ (4.2); $CO_2^+ \rightarrow C^+ + O + O$ (12.9); $CO_2^+ \rightarrow C + O^+ + O$ (15.3); $CO_2^{++} \rightarrow CO^+ + O^+$ (−18.7); $CO_2^{++} \rightarrow C^+ + O^+ + O$ (−11.5); $CO_2^{++} \rightarrow C + O^+ + O^+$ (−9.3); $CO_2^{++} \rightarrow CO^{++} + O$ (−2.3?); $CO_2^{++} \rightarrow CO + O^{++}$ (2.2); $CO_2^{++} \rightarrow C^{++} + O + O$ (−0.8?); $CO_2^{++} \rightarrow C + O^{++} + O$ (12.2). (Refs. 29, 44, 45, 52, 56, 58, 68, 79, 80.)

(6.8.1) *Carbon dioxide and hydrogen:* CO_2^+ (14.4), etc.; H_2^+ (15.9); CO^+; H^+; C^+; O^+; H_2O^+; OH^+; CH_3^+; CH_2^+; CH^+. (Ref. 60.)

(6.8.7) *Carbon dioxide and air:* See CO_2, O_2, N_2.

(6.8.17) *Phosgene:* $COCl_2^+$; $COCl^+$; CCl^+; Cl_2^+; CO^+; Cl^+; C^+; O^+; H^-; C^-; O^-; Cl^-. (Ref. 1.)

(6.16) *Carbon disulphide:* CS_2^+; CS^+; S^+; C^+. (Refs. 2, 71.)

(6.17.10) *Carbon tetrachloride and neon:* C^+; C^{++}; CH^+; CH_3^+; Cl (35)$^+$; Cl (35)$^{++}$; Cl (37)$^+$; Cl (37)$^{++}$; Cl_2^+; CCl_2^+; CCl_3^+; CCl_4^+; HCl (35)$^+$; HCl (37)$^+$; CO^+; CO^{++}; O_2^+; O_2^{++}; O^+; OH^+; Cl (35)$^-$; Cl (37)$^-$; C^-; O^-; OH^-; Ne (20)$^+$; Ne (22)$^+$. (Ref. 61.)

(7) *Nitrogen:* N_4^+; N_3^+; N_2^+ (15.65); $N^+ + N$ (22.9); $N^+ + N^+$ (33.2); $N^+ + N^+$ (37.4); $N_2^+ \rightarrow N^+ + N$ (7.5); N^{+++}; N^{++}; N_2^-; N^-. (Refs. 1, 7, 8, 17, 24, 26, 29, 33, 34, 43–45; 51, 52, 58, 59, 67, 74, 75, 84, 86.)

(7.8) *Air* (see oxygen and nitrogen): also NO^+; NO_2^+; N_2O^+; masses 56, 76, 96, 128, 140, 168, 200. (Ref. 84.)

(7.8) *Nitric oxide:* NO^+ (9.5); $O^+ + N$ (21.0); $N^+ + O$ (22.0); NO^{++} (44.0); $N^+ + O^+$ (34.5); $N^{++} + O$ (50.5); $N + O^{++}$ (55.0); $NO^+ \rightarrow N^+ + O$ (11.7); $NO^+ \rightarrow N + O^+$ (10.7); NO^-; N^-; O^-. (Refs. 22, 58, 67, 76, 79, 80, 86.)

(7.8) *Nitrous oxide:* N_2O^+ (12.9); NO^+ (15.3); $O^+ + N_2$ (16.3); $N^+ + NO$ (21.4); N_2^+. (Refs. 55, 58, 67.)

(7.8) *Nitrogen dioxide:* NO_2^+ (11.0); $O^+ + NO$ (17.7); $N^+ + O_2$ (20.8); $O^+ + NO^+$ (25.8); $O^+ + N^+ + O$ (37.8); $O^+ + O^+ + N$ (36.8); $N^{++} + O + O$ (53.8); $O^{++} + N + O$ (58.3); NO^{++}; $O^{++} + NO$ (51.8); $NO_2^+ \rightarrow NO^+ + O$ (1.3); $NO_2^{++} \rightarrow NO^{++} + O$; $NO_2^{++} \rightarrow NO + O^{++}$ (−0.2); $NO_2^{++} \rightarrow N^{++} + O + O$ (1.8); $NO_2^{++} \rightarrow N + O^{++} + O$ (6.3); NO_2^{++}; O_2^+. (Refs. 55, 58, 67, 79, 80.)

(8) *Oxygen:* O_2^+ (12.5); O^+ (20.5); $O_2^+ \rightarrow O^+ + O$ (7.5); $O_2 \rightarrow O^+ + O^+$ (33.0); O^{++} (54.5); O_3^+; O_2^-; O^-; also masses 72, 80, 100, 125, 155 and 160. (Refs. 1, 2, 3, 7, 11, 20, 24, 35, 43, 44, 45, 52, 58, 67, 76, 84, 89.)

(15.1) *Phosphine:* PH_3^+; PH_2^+; PH^+; P^+. (Ref. 1.)

(15.17) *Phosphorus trichloride:* PCl_3^+ (12.2); PCl_2^+ (12.5); PCl^+ (17.5); P^+ (22.1); PCl_2^{++}; PCl^{++}; P^{++}; Cl^+. (Ref. 96.)

(16.8) *Sulphur dioxide:* SO_2^+ (13.3); SO^+ (16.5); S^+ (16.0); O_2^+ (22.3); S^+ (21.2); O^+; $H_2SO_3^+$; masses 140 and 168. (Refs. 82, 84.)

(17) *Chlorine:* Cl_2^+ (12.3); Cl^{+4}; Cl^{+++}; Cl^{++}; Cl^+; Cl_2^-; Cl^-. (Refs. 29, 61, 97.)

(19) *Potassium:* K_2^+; K^+; K^-. (Refs. 46, 67.)

(33.17) *Arsenic trichloride:* $AsCl_3^+$ (12.3); $AsCl_2^+$ (13.0); $AsCl^+$ (17.0); As^+ (21.6); $AsCl_2^{++}$ (33.1); $AsCl^{++}$; As^{++}; Cl^+. (Ref. 96.)

(35) *Bromine:* Br_2^+(13.0); Br^+ (13.7); Br^{++} (39.5); Br_2^-; Br^-. (Ref. 92.)

(51.17) *Antimony trichloride:* $SbCl_3^+$ (11.4); $SbCl_2^+$ (12.3); $SbCl^+$ (16.4); Sb^+ (17.0, 19.8); $SbCl_2^{++}$ (32.1); $SbCl^{++}$ (34.8); Sb^{++} (38.0); Cl^+ (20.7, 24). (Ref. 96.)

(53) *Iodine:* I_2^+(9.5); I_3^+; I^+; I_3^-; I_2^-; I^-. (Refs. 29, 36, 47, 58, 67.)

(80) *Mercury:* Hg_2^+; Hg^+; Hg^{+5}; Hg^-. (Refs. 19, 30, 41, 42, 47, 48, 63.)

(80.1) *Mercury hydride:* Hg(202)H^+; Hg(204) H^+. (Ref. 89.)

(80.17) *Mercuric chloride:* $HgCl_2^+$; $HgCl^+$; Cl^-. (Ref. 9.)

(80.53) *Mercuric iodide:* HgI_2^+; HgI^+; I^-. (Ref. 9.)

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CHAPTER XVIII

IONIZATION PRODUCED DURING CHEMICAL REACTION

Introduction. Since it is possible to obtain a great variety of chemical reactions whenever ionization is produced in a material system capable of chemical change, it seems quite reasonable to expect that the reverse of the process might occur, i.e., to have ions produced while a chemical reaction is taking place. The idea is plausible, especially when the principle of microscopic reversibility is invoked, which states that any primary process which is observed must also happen in the reverse sense, i.e., when time is allowed to proceed in a reverse direction. At any rate, the idea of production of electricity accompanying chemical reactions has occurred to many individuals at various times and the phenomenon has been observed in many instances. The whole field of the electrochemistry of solutions furnishes instances of the kind discussed. Since the main interest of this monograph concerns the electrochemistry of gases, the question to be dealt with is to be restricted at once to reactions taking place in the gaseous state or at least to dielectrics of no ionizing power, and the electrochemical problems of conducting solutions are to be excluded. Otherwise the whole vast field which is usually covered by the term "electrochemistry" would have to be reviewed. The present inquiry will then be confined to the question: Are electric charges produced in chemical systems undergoing change and involving no conducting solutions? The type of change to be considered can perhaps best be defined as the limiting case of chemiluminescence. This phenomenon concerns the production of radiation during chemical change. The radiant energy originates from the reaction by having part or all of its reaction energy change into radiation. Should the energy liberated during the process be sufficient to produce ionization in any of the reactants or products, the chemical change would be accompanied by ionization and the gaseous system would show conduction in a field.

When electrolytic solutions are considered, and when it is recalled how readily the chemical energy of dissolved substances is changed into the electrical form under appropriate circumstances, it seems quite obvious that similar behavior should be found in gaseous systems. It may be stated at once that several clear-cut instances are now known where the evidence is satisfactory, and it is certain that, in systems not involving conducting solutions, ionization can result from chemical changes. In the gas reactions studied so far only very few ions are produced per molecule transformed. Most of the energy liberated during the interaction appears in the usual form of heat. In this sense the reactions of electrochemistry in solutions differ greatly from the chemical changes to be considered here, for the number of electrical charges involved in solutions differ only by a small integer from the number of molecules or atoms transformed.

The reactions to be studied suffer from a very serious difficulty which vitiates a great deal of work done in this field of research. It is always possible that frictional electricity is produced in heterogeneous systems and that the electrical charges caused by friction might be mistakenly thought to be due to chemical effects going on in the reaction mixture. For example, gas bubbles rising through a liquid can become charged electrically and the resultant electrical effect need not be caused by any chemical change occurring in the system.

On the other hand, "flames" undoubtedly are conducting, and a separation of electrical charges accompanies the reactions taking place in the flame. But the ionization occurring in flames is most probably produced indirectly by the high temperature of the process, and it is not necessarily a primary act related to the intrinsic chemical change. The rare gases can be ionized by high temperature alone and no chemical action can take place.

During the ascendancy of the ionic solution theory it was quite natural that chemists became enthusiastic along the lines proposed by Arrhenius for solutions and Thomson for gases. It became fashionable to explain all conceivable phenomena on the basis of "ionization," and no doubt this development led many investigators to seek for electrical effects in each and every province of the chemical reaction field.

Early investigations. During the eighteenth century, chemists did not make the distinction, realized later, concerning the production of electricity during a chemical reaction: galvanic or frictional. Hence it is impossible to tell in many cases whether or not the investigator had taken sufficient care to insure the absence of frictional effects. As early as 1782 Lavoisier and Laplace (1) noted that the hydrogen gas evolved when iron acts on sulphuric acid carried a positive charge. This electric charge in the gas is now known to be due to frictional effects. Other cases may be cited. For example, Pouillet (2) in 1827 reports on "the electricity of gases and atmospheric electricity" and claims that he determined, by means of electroscopes, the charges produced during the combustion of gases and solids. He draws the general conclusion that oxygen is positively charged and that the combustible gas assumes a negative charge. Such findings cannot be understood and the experiments are not satisfactory, for it is not to be expected that oxygen gas would become solely positively charged and the high temperature of the combustion would produce thermal ionization. The same author (2) finds that, on evaporating pure water from a platinum dish, no electrical effects could be noted. However, salt solutions produce charged vapors upon evaporation. Whatever the seat of the last-mentioned electrical effect, it is not due to any chemical change, as claimed, but most probably is caused by some indefinite frictional action. An interesting case of frictional electricity is reported by Armstrong, who wrote in 1840 on "the development of electricity in the steam jet of a boiler" (3, 4) and who found that the steam had a positive and the boiler a negative charge. He proposed to use such a boiler as a source of electricity, and he constructed one which would spark 33 cm. if the vapors contain a little water! However, he was not certain that friction only is the cause for this production of electricity, although Faraday (6) and Buff (5) stated this belief.

A century ago many scientific workers thought that electricity could be produced when gases interacted with solids. For example, de la Rive (7) summarizes his views on the matter as follows: (1) When two heterogeneous bodies in contact are placed in a liquid *or a gas* which has a chemical effect on them, electricity is produced. (2) Simple contact, where there is no chemical action, does not produce electricity. (3) The electricity developed depends on the nature of the action and recombinations and not on the vivacity of the action. Statement (1) cannot be accepted unless the reference to a gaseous medium be deleted, for it will be shown that the type of action implied is most difficult to detect. However, other investigators, at the same time, held that electricity could be produced by simple contact of bodies without the intervention of chemical action. This view was expressed by Peclet (8).

Types of reactions. The experimental evidence obtained by investigators studying the production of ionization usually involved the demonstration that some electrical system had become charged by contact with the nascent gas produced during the reaction. It was early recognized that gases bubbling through liquids can become charged electrically by friction and at times such charges would last a considerable period after creation. These charges were further found to be responsible for the formation of clouds of fog whereby the ions present served as nuclei for the condensation of vapor. Some investigators believed that the whole of the electrical phenomenon produced in the reactions studied was due to frictional effects entirely; another school of thought maintained that at least part of the charges evolved were caused by the chemical reaction. Naturally many controversies arose. It is clear that it would be difficult to avoid all frictional effects and to produce a crucial demonstration of the electrical action sought. De Broglie and Brizard (9) contend that any electrical effects accompanying chemical reactions are altogether of a physical nature and not directly connected with any chemical change. They state that in reactions without rupture of the liquid or crystalline surface, as in reactions between gases in the cold, double decompositions and dry decompositions of amorphous powders, no charged ions are produced. In vigorous reactions, where liquids splash about, ionization may occur, depending on the liquid. Whenever liquid or crystalline surfaces are ruptured during a chemical reaction, ions appear. Hence they are due to physical phenomena concomitant with the chemical change. For example, the hydration and dehydration of quinine sulphate is accompanied by the appearance of electrical charges in the surrounding air. The phenomenon is most probably due to frictional effects produced during the rupture of the crystals (10, 11). Bloch (12) studied the displacement of hydrogen from dry hydrogen chloride and from hydrochloric acid by zinc and found no electrical effects in the dry reaction. He supposed the charges formed during the wet reaction to be due to the surface effects, such as bubble formation, liquid films breaking, etc. He showed (12) further that pulverizing liquids causes them to become charged and that their relative activity is the same as in bubbling a gas through them.

Pinkus (86) and Brewer (84), on the other hand, believe that ions are produced while certain chemical reactions take place, but Trautz and Henglein (80) cannot find electrification with chemical reaction. Dhar (32) thinks that even induced oxidations are initiated by ions produced by the primary reactants. Brewer (84) proposes a completely ionic theory of surface catalysis. Since emission of ions has been found near the surface during several surface-catalyzed reactions, it is supposed that all catalytic surface reactions take place in the gas phase near the surface, via an ionic mechanism. However, it seems unnecessary to assume complete ionization of reactants when their dissociation into neutral atoms and radicals is sufficient to explain the catalytic effect of certain surfaces. Moreover Schmidt (87) very definitely points out that no hydrogen ions need be expected by thermal emission from any surface at usual temperatures. The ionization potential of hydrogen molecule or atom is much too large to expect such ions. Only alkali ions are usually emitted from surfaces because their ionization potentials are small in comparison to the work function of the usual surface material. It is most probable that hydrogenation catalysis does not take place by an ionic mechanism but involves hydrogen atoms produced by activated adsorption.

A great variety of chemical reactions have been inspected for electrical effects. Many conflicting reports have been made by various investigators over a period of a century. In most cases frictional electrical effects must be considered responsible, as the systems involve heterogeneous phases, such as liquids and gases. The hydrogen gas released from sulphuric acid is said to be charged positively (1). Ions are produced according to Helmholtz and Richarz (13) when hydrogen chloride gas and ammonia combine to form ammonium chloride mist, during the oxidation of ammonia gas by ozone, the interaction of nitric oxide and water, the oxidation of nitric oxide and phosphorus, the displacement of hydrogen in water by alkali metals and the decomposition of ozone. On the other hand, no action of an electrical nature was found during the reaction of sodium nitrite and sulphuric acid and the decomposition of nitrous acid into water and nitrogen trioxide. The gases released during the electrolysis of solutions of sulphuric acid, sodium hydroxide, potassium iodide and hydrogen chloride were reported charged by Townsend (14), while Thomson (15) could discover no ions during the reaction of hydrogen with moist chlorine gas, nor Guggenheimer (16) for the oxidation of hydrogen peroxide by moist oxygen gas. However, Coehn (17) reports positive ions during the decomposition of ammonium amalgam (NH_4) though other amalgams showed no effect. The decomposition of potassium permanganate into manganate, manganese dioxide and oxygen gas is accompanied by ion emission of only one ion per 2.3×10^{12} molecules reacting, according to the finding of Cunningham and Mukerji (18). Similarily potassium chlorate and perchlorate, sodium peroxide and mercuric oxide show respectively one ion per 0.6, 1.0, 4.3 and 9.0 ($\times 10^{12}$) molecules decomposed, and the formation of boron nitride from borax and ammonium chloride is said to release negative particles (19). But then again Reboul (20) reports no ion emission during the neutralization of acids and bases, the mixing of sulphuric acid and water and metatheses with precipitation. He states that positive ions are formed, in excess, by frictional processes in reactions with gas evolution, when metals act on acids or water reacts with anhydrides and when ammonium amalgam decomposes. Negative ions are similarly formed by friction during heterogeneous reaction such as the oxidation of aluminum amalgam by moist air, the reaction of fresh surfaces of potassium or sodium with oxygen gas, the displacement of hydrogen in hydrogen sulphide gas by silver and sodium, the combination of potassium oxide and carbon dioxide as well as reduction of nitrogen dioxide by metallic copper. Reboul also finds ions in the gas phase during the interaction of hydrogen chloride and ammonia and the oxidation of hydrogen sulphide by oxides of nitrogen. But the formation of ammonium chloride from the dry gases does not involve electrical charges, and lead carbonate and mercuric oxide behave similarly. However, the decrepitation of crystals of sodium and potassium chloride, potassium bromide and iodide and lead nitrate shows the formation of charged particles. And the fumes arising during the mixing of sulphur trioxide and water, of phosphorus pentachloride and water and of sulphur dioxide and moist air are also charged electrically. Then again no charges were found by de Broglie and Brizard (9) during the action of moist air on phosphorus pentachloride and trichloride, nitric acid, phosphorus pentoxide, arsenic trichloride, silicon tetrafluoride, sulphur trioxide, hydrogen chloride and bromide. Nor could they discover any concomitant electrical phenomena during the formation of ammonium chloride. The formation of arsenic and antimony chlorides from the elements, the decomposition of permanganate and the interaction of zinc and dry hydrogen chloride produced no separation of charges, while the last-named reaction creates electrical charges when the gas is wet. The last-mentioned reaction was investigated by Bloch (12). Essentially similar changes have been studied by others (21-30), and it appears that in much of the earlier work frictional effects were not excluded with sufficient care.

Alkali metal reactions. Thomson (33) showed that rubidium-potassium and sodium-potassium alloys give off negative particles of electricity and that this discharge is greatly increased in the presence of hydrogen. Carbon dioxide and air do not have this effect. During the adsorption of hydrogen a definite separation of electricity takes place. Reboul (20, 31) found that potassium and sodium metals, while being oxidized by moist air, produced charges of both signs and the negative ions predominated. Alkali amalgam behaved in similar fashion. A slight increase in temperature caused a much greater effect. This large negative charge did not seem explainable on the view that friction or temperature was the sole cause of the production of electricity. Sodium and chlorine reacted, and the charges increased with the extracting field.

Reboul also studied the question whether or not the flame accompanying certain reactions was a necessary concomitant of ionization. He observed the chlorination of arsenic, antimony, selenium, tin and iodine with and without dilution by an inert gas, and he found much less ionization in the reaction when proceeding without ignition. Dunoyer (34) studied rubidium and found a current in total darkness which increased enormously when light fell on the metal. He supposed that infra-red rays caused the dark phenomenon. It is possible that the effect observed by Thomson and Dunoyer may have been due to the radioactivity of potassium and rubidium as later discovered by Campbell and Wood (35). The lack of action by carbon dioxide and air may have been due to the fact that the skin of acids, formed early, during the introduction of the alkali metals, prevented further interaction. This possibility was pointed out by Haber and Just (36).

The work of Haber and Just. These investigators took up the problem of ion production during chemical action and they found (36) that a liquid sodium-potassium alloy gave off electrons when the oxide skin was scraped off with a razor or a glass rod while in an electrical field. The new surface so created could react again with the surrounding air, and the chemical action appeared to be accompanied by the emission of electricity. The effect was compared to the photoelectric effect because radiation falling on the surface of an alkali metal also liberated electrons. That the chemical effect was not simply a photoelectric phenomenon, however, was shown by carrying out the experiment in a dark room, where the electron emission occurred just the same. The first thought in an attempt at explanation would perhaps be to suppose that the friction of scraping caused the emission of electrons from the surface of the metal. However, it was observed that the maximum electrical effect sometimes occurred a little while after the scraping had been stopped and that the surface became dull in appearance after the passage of time. This situation would indicate that the friction of the scraping is not the immediate cause of the appearance of electrical charges, but that the subsequent chemical reaction is indeed accompanied by a liberation of electrons. The field in these experiments was so directed that electrons were drawn from the surface. With the field reversed a much smaller effect was noticed. With no field the effect was not noticeable. However, a current of air blown over the amalgam surface caused it to assume a positive charge, i.e., electrons were blown away from it. The initial velocities of the electrons were found to be very small.

No quantitative study of the amount of chemical action, as compared to the number of electrons liberated, had been made, and the experiments do not exclude the possibility of frictional effects with the exception of the observation of the lag noticed in some of the runs where the charging-up and the chemical action occurred after the scraping had been performed. This lag seemed difficult to explain on a frictional basis.

Haber and Just (37) showed further that hydrogen and nitrogen are two gases which did not react chemically with sodium-potassium alloy, and they were also unable to obtain electrical charges from the alloy surface when these non-reacting gases came in contact with it. The same gases, when moist, showed a chemical effect, and then the separation of charges occurred in the sense that electrons were liberated from the reacting surface. Hydrogen chloride, iodine vapor, oxygen, sulphuryl chloride, and phosgene reacted with the alloy surface, and in every case electrons were emitted. With the extracting field reversed no positive charges were observed.

Such studies were continued by Haber and Just (36) with vapors of phosgene acting on sodium-potassium alloys in the dark and at room temperature. The pressures of phosgene used were very small, and again it was found that the alloy surface took a positive potential of 1 volt, i.e., electrons left it. The nature of the particles leaving the surface was determined by a magnetic field. Bromine vapor acting on the liquid sodium-potassium alloy also liberated electrons. When, however, the potassium amalgam was replaced by amalgams of cesium and potassium or lithium negative ions were liberated from the reaction surface. The amalgams were allowed to drop from a metal capillary tip, great care being taken to avoid the formation of films which would prevent the liberation of charge. Dry nitrogen had no effect, which points against the possible belief that frictional effects might serve for the production of the charges liberated. One electron was liberated per 1600 molecules reacting.

The combined effect of light and chemical action was studied by Haber and Just (38). It was found that the combined action on a sodium-potassium alloy was greater than the sum of the individual effects. They also studied other surfaces such as copper, aluminum and silver at higher temperatures (200° C.), and they observed the emission of electrons when hydrogen chloride and iodine vapor were allowed to react with these surfaces.

Considering the work on alkali alloys it seems definite enough to show that the production of electrical charges during chemical reaction is indeed observable. Frictional effects are no doubt responsible in many cases. The reaction between alkali metal amalgams and various gases is the most clear-cut instance reported, so far, of the phenomenon under discussion.

The researches of Richardson and his co-workers. The study of electron emission during chemical reaction was taken up by Richardson

(39), who, following Haber and Just (38), commenced a series of researches on sodium-potassium alloys under the influence of various gases. Richardson and his co-workers carried on a most careful set of investigations, and it may be said that they advanced the subject onto a very firm and definite basis, so that the age-old question whether or not there is an electrical effect accompanying chemical reaction may be answered more definitely than ever in the affirmative. Independent of frictional effects there was found electron emission from an alloy surface when acted upon by various gases. Richardson and his workers check Haber and Just on this point.

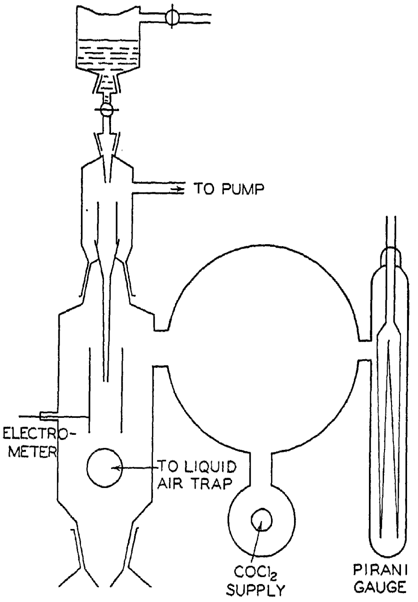

FIG. 75.—Apparatus for study of electron emission from liquid alloys while reacting chemically with various gases. Denisoff and Richardson, Proc. Roy. Soc. **A132**, 22 (1931).

The earlier investigations (39, 40, 41) showed that the experiments needed to be carried out at low pressure (10^{-7} to 10^{-5} mm.) and that the accurate measurement of these pressures was of the greatest importance. Contact potentials were troublesome to estimate, and many other details such as size of drop of the liquid alloy, duration of dropping, etc., had to be studied. In the earlier work it was thought that the electrons emitted from the surface of the drops under the influence of a gas, usually carbonyl chloride ($COCl_2$), had Maxwellian velocity distribution, and naturally the mean temperature of this distribution was calculated. It was usually found to be between 2000 and 3000° K. Later, however, it was recognized that the distribution was not truly of the Maxwell type, especially as the higher-speed electrons were measured with greater care.

Richardson and Grimmett (42) found the electron emission to be a function of the pressure of the gas attacking the alloy. The efficiency of the process was low: only one ion (electron) was emitted per 10^7 molecules reacting on the surface.

Low-pressure reactions. The investigations which Denisoff and Richardson (43) have carried on lately are an example of the most careful and painstaking high-vacuum research possible with modern technique. They developed the measurement of low gas pressures and their manipulation, under very trying conditions, at pressures from 2×10^{-7} to 10^{-2} mm. Hg. They insured uniform feeding of the liquid alloy through the nozzle (Fig. 75) and they arranged for heating of the outer electrode so as to avoid deposition of alloy and consequent changes in contact potential.

With their improved technique they found that, in the pressure range from 2×10^{-7} mm. to 10^{-5} mm., the total electron emission from the NaK_2 surface is proportional to the pressure of the carbonyl chloride present in the reaction chamber. At about 3×10^{-5} mm. the emission has a sharp maximum followed by a decrease which reaches constancy at 10^{-3}-mm. pressure. At the maximum value of the current the alloy surface was covered with a more or less complete layer of the product. It was found that one electron was ejected per 14,000 molecules reacting on the surface. It will be recalled that Haber and Just (36) found this number to be 1600.

Twenty-two gases were studied by Denisoff and Richardson (43), and the different effects on the K_2Na alloy were noted. With fifteen gases the emission of electrons during chemical action was sufficiently large to permit the determination of the velocity distribution. The pressures of the reacting gases were of the order of 10^{-5} mm. Hg. The important conclusions these authors arrived at in these latest researches are the following:

1. The distribution of energy of the chemically emitted electrons is non-Maxwellian.
2. The maximum energy which they may possess is difficult to define and observe, but a maximum exists as in the photoelectric effect.
3. Most of the electrons (99.9%) have energy below a value E_m defined as the practical maximum energy.
4. For chlorine compounds a simple relation exists between the heat of dissociation D of the compound and E_m:

$$E_m + D = \text{const.}$$

5. The yield of electrons per unit pressure decreases rapidly as the energy of the reaction diminishes.

These facts can be accounted for by an hypothesis involving a triple collision between the reaction partners and a free electron, which carries off the energy. The surface reaction may be indicated to be:

$$2K(\text{surface}) + COCl_2(\text{gas}) + E^-(\text{slow}) \rightarrow 2KCl + CO(\text{gas}) + E^-(\text{fast}).$$

Of course a great many of the interactions between alloy and gas may occur in the usual way with the excess of energy appearing as the heat of reaction:

$$2K(\text{surface}) + COCl_2(\text{gas}) \rightarrow 2KCl + CO(\text{gas}) + \text{Heat}.$$

Since the fast electron will have to leave the surface of the alloy, and since its energy must come from the energy resulting from the chemical reaction, it is understandable that the relation

$$E_m = E_c - \phi$$

should hold, where E_c is the energy corresponding to the elementary chemical reaction step, ϕ is the work function of the metal and E_m is the maximum value of the energy of the escaping electrons. Denisoff and Richardson point out that this relation appears to be general, and it is noted that it is analogous to the fundamental law concerning the behavior of photoelectrons.

A calculation of the energy of the surface reaction (E_c) between phosgene and potassium yields 5.25 e.v. Since the work function of the alloy used is 2.5 e.v., it follows that the maximum possible value for the energy of the emitted electrons is

$$)_{\text{max.}} = 2.75 \text{ e.v.}$$

The observed values of E_m lie between 2.52 and 3.05 e.v.

The reaction between phosgene and alkali metal atom might be a two-stage process:

$$K + COCl_2 \rightarrow Cl^-(\text{on metal}) + COCl; K + COCl \rightarrow Cl^-(\text{on metal}) + CO$$

This possibility is considered by Denisoff and Richardson (43) with the result that they exclude this mechanism, because the calculated maximum energies of the expelled electrons do not agree with the experimental values. In the case of nitrosyl chloride (NOCl) a one-stage mechanism is the only one possible and the calculated value of the maximum electron energy (2.9 e.v.) agrees with the experimental value of 2.6 to 3.1 e.v. For chlorine the reaction appears to be one-stage:

$$K + Cl_2 \rightarrow 2Cl^- \text{ (on metal)}$$

On the other hand, bromine and iodine seem to interact with the alloy in a two-stage interaction such as:

$$K + Br_2 \rightarrow Br^- \text{ (on metal)} + Br;\ K + Br \rightarrow Br^- \text{ (on metal)}$$

The work of Denisoff and Richardson can be summarized by comparing the observed and calculated maximum electron energies (Table 26). Of further interest is the yield expressed in electron current (amperes) per unit pressure of reacting gas as the pressure tends to zero. The highest yield (for Cl_2) is equivalent to the emission of 1.5×10^{-4} electron for each adsorbed atom of chlorine. The emission of electrons is small with hydrogen chloride and water vapor and probably zero with nitrous oxide. Similar studies on sulphur chloride (S_2Cl_2), thionyl chloride ($SOCl_2$), mercuric chloride ($HgCl_2$) and sulphuryl chloride (SO_2Cl_2) led to a consideration of specific yields of one- and two-step reaction mechanisms and a definition of a composite yield pertaining to these reactions (43). In mixtures of gases the emission currents are additive; they exhibit saturation with true zero applied potential difference. In the range of 3.0 to 0.7 e.v. of the energy available in the corresponding elementary reaction mechanism (E_c), the number of electrons emitted per chlorine atom

TABLE 26

ENERGIES AND YIELD OF ELECTRONS

A. K. Denisoff and O. W. Richardson, Proc. Roy. Soc. **A145**, 18 (1934).

Gas	E_c Volts (calculated)	E_m Volts (calculated)	E_m Volts (observed)	Yield Amp./mm. $\times 10^4$
Cl_2..........	5.77	3.27	2.80	20 (25)
NOCl.........	5.43	2.93	2.60	7 (10)
$COCl_2$........	5.25	2.75	2.55	2 (3)
HCl..........	2.64	.14	......	0.002
Br_2..........	4.50	2.00	1.75	2 (5)
I_2...........	4.36	1.86	1.5	0.3 (0.4)
COS..........	4.10	1.60	ca 1.0	ca 0.00003
H_2O..........	....	....	......	0.0_53
N_2O..........	....	....	No reaction	0.0_62

reacting is an exponential function of E_c. The most frequent mechanism is one in which only one of the two available chlorine atoms reacts.

Theoretical treatment. The theory of the energy distribution of the electrons emitted during chemical reaction and the absolute value of the oxidation from alloy surfaces (NaK_2) are given by Denisoff and Richardson (43) along the lines indicated herewith. The process of interaction between the gaseous molecule and the surface can be described by considering the action to be the approach of a chlorine atom of the chlorine-containing gas molecule to a potassium atom bound to the surface. When these two atoms approach within a certain distance they may be considered to form an excited (energy rich) non-polar bond. The possibility exists that the two atoms revert to an ordinary ionic bond of the product (KCl), and the energy E (Fig. 76) is given to a free electron of the metal, because this electron happened to be interacting with the two atoms (K and Cl) while they were in the excited state. It is seen then that the electron emission is looked upon as an immediate result of collisions of the second kind between free metallic electrons and the electronically excited chemical bonds formed by the gas molecules on the alloy surface. As far as free metallic electrons are concerned it is clear that their behavior must be considered on the basis of the modern electron theory of metals as developed by Sommerfeld. The experimental electron

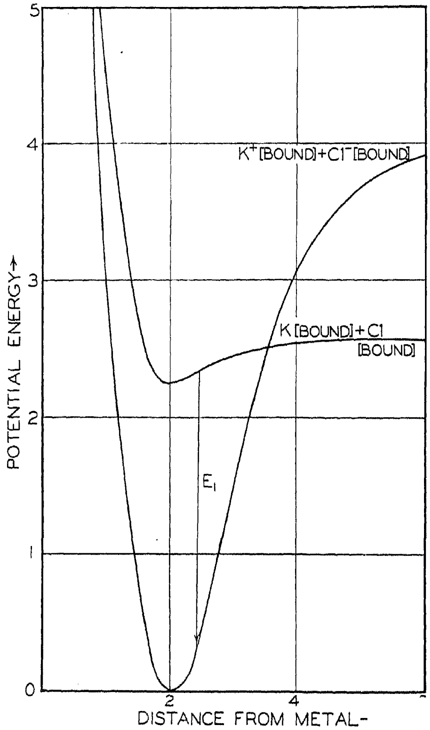

FIG. 76.—Potential energy of the chlorine atom bound on the alloy surface. Denisoff and Richardson, Proc. Roy. Soc. **A148**, 533 (1935).

energy distribution curves can be discussed by means of a de-excitation function which has the interesting property of making the energy distribution of the emitted electrons nearly Maxwellian for small values of the energy *E*. This situation explains the earlier deductions of Richardson and his co-workers, where they considered the emitted electrons to have a Maxwell velocity distribution. Another interesting result of these researches is the determination of the total potential barrier of the alkali surface NaK_2. The value found is 5.0 e.v., which compares well with the calculated values of 4.28 e.v. for potassium, and 5.70 e.v. for sodium.

Denisoff and Richardson (43) tested the theory of electron production during chemical reaction further by a study of the heterogeneous reaction between the usual sodium-potassium (NaK_2) alloy and the following gases: cyanogen chloride, mercuric bromide, hydrogen peroxide and ozone. At very low pressures these gases produce a measurable current of electrons leaving the metals. The gases methyl chloride, cyanogen, mercuric cyanide and hydrogen sulphide give only a very small emission. These authors realize that the halogen atoms and other radicals and atoms released during these reactions possess an electron affinity and that therefore the possibility exists that they may appear as negative ions in the current from the alloy. Although Haber and Just (36) have shown that their currents were mostly, if not altogether, electrons, it is necessary to prove this point by further appropriate experiments.

The work on the heterogeneous interaction of alkali metal alloys and various gases shows quite clearly that it is possible to have electrons liberated by impacts of the second kind while chemical reactions take place. On the principle of microscopic reversibility the reverse of such a process must also be possible, and it may be expected that electrons can activate a chemical system and cause it to undergo chemical change. This last-mentioned process is, of course, the one more easily and hence more usually observed.

Slow oxidation of phosphorus. Of the many chemical reactions which have been studied for years for the purpose of finding concomitant ionization, the slow oxidation of phosphorus seems to be another authentic case. The reaction must be considered at low temperature only, for, should vigorous oxidation ensue and flame conditions be approached, the resulting high temperature would necessarily produce ionization. The first observation is credited to Matteucci (1, 44). Harms (45), Trautz (46) and Richardson (1) have reviewed the earlier investigations. Among others, Harms (45) found that very few ions are formed during the oxidation: only one ion was found per 10^8

molecules of oxygen used. No other gas but oxygen causes the electrical effects noted, and it is certain that the ionization is in some way connected with the process of oxidation (47). The actual ion-producing act may be of only secondary nature, for other oxidations do not show any ion production. The luminescence observed during the oxidation might contain ultraviolet components which by a photoelectric effect could cause the production of ions. However, this possibility is ruled out by Meyer and Müller (47). They also noted that certain vapors such as carbon disulphide which tend to stop the oxidation also stop the production of ions. Schenck, Mihr and Banthien (48) discovered a variety of substances which acted like carbon disulphide when mixed with air. The ionization of the air was less after these substances had been in contact with yellow phosphorus. But if the air had passed over phosphorus first and then was allowed to pass over or bubble through terpene oil, alcohol or mesitylene, etc., then the ionization was not destroyed. This experiment showed that the ionization once produced was not affected by these negative catalysts.

Influence of water vapor. Water vapor has a decided influence upon the course of the oxidation of phosphorus. A certain optimum pressure of water is best for the production of ions, depending upon temperature and oxygen pressure. Greater or lesser humidity is unfavorable to ionization. However, according to Busse (49), it appears that oxygen dried for some time with phosphorus pentoxide still does oxidize yellow phosphorus, even though but slowly. The temperature at which oxidation commences in air is dependent on the humidity of the air. The ionization parallels the oxidation. There is a maximum yield of ions as there is also a maximum of the rate of oxidation, according to Russell (50). Tausz and Görlacher (51) found that, when phosphorus is oxidized with air, the ionization increased with air velocity, temperature and phosphorous surface. Pure, wet oxygen showed no increased ionization over air, but a progressive increase in electrical conductivity was noted upon drying. Catalytic poisons, such as cyclohexane and isoprene, when mixed with air, caused considerable decrease in the number of ions produced. The effect depended on the concentration of the poisons.

Ozone mechanism. Schönbein (52) was the first to show that ozone formation accompanies the slow oxidation of phosphorus. It was quite natural then that later investigators, for example Guggenheimer (16), would advance the idea that the ozone formed might be involved in the production of the electrical charges. However, further research, such as that by Schenck, Mihr and Banthien (48), showed that the ozone can be formed, and used in further oxidation processes, without involving electrical phenomena. The number of ozone molecules produced in phosphorus oxidation is of about the same order of magnitude as the number of oxygen molecules disappearing, whereas the number of ions produced is of a much lower order, as mentioned above. In general, oxidations accomplished by means of ozone or hydrogen peroxide do not show ionization.

Other modifications of phosphorus. Landin (53) states that amorphous phosphorus ionizes the surrounding air on oxidation. He claims that, though the ionization is weak at room temperature, it becomes strong upon ignition. Of course such a high-temperature reaction cannot be considered a proper case in point. Similar results were reported by Schenck, Mihr and Banthien (48), but Busse (49) does not substantiate these findings. It seems established that only yellow phosphorus on slow oxidation shows electrical effects.

Phosphorus trioxide. The products of the slow oxidation of phosphorus are ozone, phosphorus pentoxide and phosphorus trioxide. The last substance was prepared by Schenck, Mihr and Banthien (48) and tested for ionization. Hydrogen gas, passing over molten trioxide, would discharge an electroscope, and air acted even more vigorously. It is the presence then of phosphorus trioxide vapors (P_4O_6) which produces the conductance of the air in the neighborhood of the oxidizing phosphorus. During the further oxidation of the trioxide the same luminosity but no ozone appears, as has been shown by Thorpe and Tutton (54). Under certain conditions the luminosity may be intermittent in nature, and the oxygen pressure has lower and upper limits depending on temperature. Schenck, Mihr and Banthien (48) determined the vapor pressure of phosphorus trioxide (P_4O_6) and showed that its oxidation depends on the square root of the oxygen pressure, indicating that oxygen atoms are involved in the process. Later Schenck and Breuning (55) decided that the interaction of phosphorus trioxide and oxygen is not responsible for ion production but that the hydration of the oxide produces the ions observed. The reaction with water, however, is not simply the formation of phosphorous acid, for Schenck and Breuning found a yellow deposit which they guess may have been a solid phosphorus hydride ($P_{12}H_6$). They tried to determine more definitely the nature of the substance responsible for the ionization, but they were only able to say that it can be condensed at the temperature of liquid air.

Rinde (56) studied the luminescence and ionization of phosphorus trioxide vapor in mixtures of various gases, mostly carbon dioxide and oxygen. Since no light is emitted in carbon dioxide the oxidation of phosphorus trioxide is evidently involved in the chemiluminescent process. The intensity of radiation increases with the partial pressure of oxygen up to 5%; further increase in the relative amount of oxygen rather diminishes the emission of light. The results with dry and moist gas indicate that the oxidation proceeds according to the reactions:

$$P_4O_6 + 2O_2 \rightarrow 2P_2O_5$$

$$P_4O_6 + 6H_2O + 2O_2 \rightarrow \text{Intermediate products} \rightarrow 4H_3PO_4$$

No difference is found between the mobilities of the positive and negative ions formed in the process. Only very few ions are formed per reacting oxygen molecule. When copper electrodes are used for the electrical measurements, both the luminescence and ionization cease and a black deposit appears on the copper surface; thus the intermediate compound formed from phosphorus trioxide and water vapor reacts with copper more readily than it undergoes oxidation.

Ion mobility. Przibram (57) determined the charge on the fog particles produced during the oxidation of phosphorus with air. The radii of these drops are of the order of 10^{-5} cm., their charges are multiples of 4.7×10^{-10} e.s.u. and they lie between the limits of 1.8 and 110×10^{-10} e.s.u. These droplets are most probably formed by the condensation of water vapor on the initial ions resulting from the chemical reaction. Another determination of mobilities was made by McClelland and Nolan (58), who claim to have found fourteen different kinds of ions ranging in mobility from 0.22 to 0.000053 cm./sec. per volt/cm. Positive and negative ions were present in about equal numbers. On the other hand, Busse (49, 59) found that the ions obtained downstream in a current of air under a temperature gradient (40 to 20° C.) showed a practically continuous spectrum as to mobility. The values ranged from 1 to 0.001 cm./sec. per volt/cm. for the positive ions and from 8 to 0.001 cm./sec. per volt/cm. for the negative ions. The mobilities of the ions changed with age. It is seen that the negative ions were eight times faster than the positive ones. Busse concluded that the negative ions must carry a higher charge than the positive ones. Water vapor was essential. Photoelectric action did not account for the production of ions, for one would expect then that positive ions of even higher charge should appear. It seems that these experiments can best be interpreted on the theory that an acid of phosphorus produced during the oxidation process is responsible for the electrical effect. Perhaps the best guess is the hypothesis that dimolecular pyrophosphoric acid $(H_4P_2O_7)_2$ is responsible for the ion production. By electrolytic dissociation an eightfold charged ion would at least be possible, according to Busse.

The spectrum of the luminescence. In order to determine the carriers of the phosphorus luminescence, Petrikaln (60) determined the emission and absorption spectra of phosphorus pentoxide and phosphorus trioxide. Upon excitation with electrons the pentoxide shows only the spectrum of oxygen due to decomposition of the oxide. Phosphorus pentoxide showed no absorption in the ultraviolet (2100 Å), and probably its emission spectrum is located in the Schumann region.

On the other hand, the spectrum of the trioxide obtained by electron excitation consists of a band spectrum which is found to be completely identical with the well-known phosphorus luminescence. The trioxide has a continuous spectrum in the visible region and two band systems. The continuous spectrum may be due to the pentoxide.

The phosphorus luminescence is probably produced by the transfer of energy to trioxide molecules during the oxidation to pentoxide with the intervention of a particle M which transfers the kinetic energy:

$$P_2O_3 + O_2 + M \rightarrow P_2O_5 + M \text{ (295 k-cal.)}$$

$$P_2O_3 + M \text{ (295 k-cal.)} \rightarrow P_2O_3{}^* + M$$

$$P_2O_3{}^* \rightarrow P_2O_3 + h\nu \text{ (luminescence)}$$

or

$$P_2O_3 + O_2 \rightarrow P_2O_5 + \mathrm{h}\nu'$$

$$h\nu' + P_2O_3 \rightarrow P_2O_3{}^*$$

$$P_2O_3{}^* \rightarrow P_2O_3 + h\nu$$

The energy of the oxidation process may be transferred to another trioxide molecule either by impacts of the second kind or by radiation. Since the oxidation of phosphorus and of the trioxide gives the same luminescence, it is clear that the oxidation of phosphorus to the trioxide is not involved in the process of light production. Furthermore, investigation by Weiser and Garrison (61) support this view. They found a very rapid oxidation of phosphorus to the trioxide at 27° C., whereas the further oxidation to the pentoxide became prominent only at 65° C. This result must mean that the oxidation products of phosphorus, as usually carried out, will contain great quantities of trioxide molecules. The transfer of energy as outlined above should then easily be possible. Since the energy of the oxidation of the trioxide to the pentoxide amounts to 295 k-cal. per mole there is plenty of energy available not only to excite the trioxide molecules but most probably to ionize them as well:

$$P_2O_3 + O_2 + M \rightarrow P_2O_5 + M \text{ (295 k-cal.)}$$

$$P_2O_3 + M \text{ (295 k-cal.)} \rightarrow P_2O_3^+ + E^- + M$$

and in this way the ionization observed during the oxidation may be produced.

Adsorption layers. A variety of heterogeneous reactions will be discussed below, where the electrical conductivity of the gas phase during reaction has been determined. The view is held that these reactions are surface-catalyzed by the electrode walls, and since electrical effects are observed it is supposed that the mechanism involves ions on the surface. From the general point of view of contact or surface catalysis the condition of gas molecules on solid surfaces is, of course, of greatest importance. If evidence can be produced that ions are involved in heterogeneous catalysis, such findings must be considered in a complete picture of the theory of catalysis.

It is therefore of great interest to report certain researches which tend to show that surfaces show electrical effects under certain conditions. The question asked very early was naturally in regard to the new condition which the adsorbed gas molecules had attained on the adsorbing surface, which made it possible for them to undergo reactions at such remarkably increased rates. The adsorbed molecules must be activated to some new state which can undergo reaction much more easily than the ordinary configurations known in the gas phase. Three possibilities come to mind at once: the molecules must be in some higher energy state, i.e., they must be either electronically or vibrationally or rotationally excited; or they must be dissociated into atoms or radicals; or they must be ionized into charged parts. It is this last possibility which is of interest at the moment. No attempt therefore will be made at a complete critical survey of the development of ideas in the whole field of contact catalysis. Only researches which deal with the possible adsorption of gas ions will be considered.

In an investigation on the combustion of hydrogen in contact with hot surfaces Bone and Wheeler (62) noted the catalytic effect of various solid materials. They suggest the possibility of a difference of opinion as to the mechanism of the contact action. It may be supposed that the catalyst dissociates the hydrogen molecules into atoms:

$$H_2\text{(gas)} + \text{Surface} \rightarrow 2H \text{ (on surface)}$$

or it may be that actually ions are produced:

$$H_2(\text{gas}) + \text{Surface} \rightarrow 2H^+ + 2E^- \text{ (on surface)}$$

They noted that hydrogen has a greater effect on the electron emission of platinum than does air, as found by physicists. The emission of electrons is 25,000 times greater in the first gas than in air at 0.014 mm. pressure. Thomson (63) had shown that the alkali metals have their electron emission greatly increased while absorbing hydrogen. These facts point to a great effect of gas adsorption on the electrical properties of various surfaces. However, it must be noted that the temperatures used when electron emission of surfaces is studied are usually much higher than the temperatures employed in the investigation of catalytic processes. Kirkby (64) also suggests the possibility of an electrical effect when platinum at 275° C. catalyzes the hydrogen-oxygen combination, and Thomson (65, 66) considers "that it is not improbable that the emission of electrified particles from the surface of a catalyst is a factor of primary importance in its behavior. The action of surfaces may ultimately be found to depend on the fact that they form a support for layers of electrified gas in which chemical changes proceed with high velocity."

Following the suggestion of Bone and Wheeler (62), Hartley (67) studied the electrical condition of a gold surface during the absorption of gases and their catalytic combustion. He found that a gold surface acquired a negative charge during catalytic combustion (at 350° C.). This electrical effect is probably antecedent to the combustion proper and is mainly a phenomenon of gas occlusion. The metal was found to become negatively charged during the adsorption of hydrogen and carbon monoxide and positively charged when oxygen gas was placed in contact with it. These electrical effects of hot metal surfaces were studied further by Finch and Stimson (68), who extended the work of Hartley (67) to silver. They also worked over a wider temperature range (to 850° C.), and studied oxygen, hydrogen, their mixtures, carbon dioxide, carbon monoxide, nitrogen and argon. The gold and silver surfaces became charged when heated in contact with a gas or in high vacuum (10^{-5} mm. Hg.) The magnitude of the charge depends upon the nature of the gas, the temperature and the history of the metal. It does not depend upon the gas pressure. Evacuation of the gases would bring back the vacuum conditions of charges. Oxygen and air on gold or silver and hydrogen on silver are strongly absorbed so that from 12 to 48 hours were required to reestablish vacuum conditions of surface charge. The other gases could be removed in much shorter periods (2 min. to 2 hours). Raising the temperature increased the rate of charge removal. The oxygen charge on silver or gold and the hydrogen charge on silver could be removed in 5 min. by allowing hydrogen or oxygen respectively to come in contact with the charged and gas-covered metal. The value of the charge due to water vapor was the same as that due to a mixture of hydrogen and oxygen. The previous heat treatment of the metal surface had a profound retarding effect upon its later activation. It should be noted that Finch and Stimson used no flow system. They admitted the gases to the reaction chamber containing the metal sheet or gauze, and made their electrical measurements while the body of gas was at rest. It seems then that ordinary frictional effects were absent. They surmise that the gas molecules are dissociated into ions on the surface of the metal. The same authors (68) studied the electrical charges on a nickel cylinder when heated in vacuum and when exposed to oxygen, hydrogen, their mixture, carbon dioxide, water vapor, nitrogen, argon and mixtures of these gases. In general the phenomena observed were the same as with gold and silver surfaces. After the surface had been " normalized " by several successive oxidations and reductions, the charge due to a given gas is characteristic of the gas and the temperature and it is independent of the pressure. The nickel surface becomes oxidized in oxygen, but the oxide surface has the same vacuum charge as the reduced oxygen-free surface. The value of the charge due to a reaction product is identical, at all temperatures, with that of the original mixture. Argon and nitrogen diluted with 2% of hydrogen or oxygen give the full value of the charge due to either one of the latter gases, showing that hydrogen and oxygen have a much greater influence on the nickel surface than argon and nitrogen have. These experiments show that at least some of the molecules of adsorbed gases are in a different electrical state, i.e., are ionized when adsorbed on metal surfaces. Finch and Stimson realize, of course, the importance of these experiments in connection with the general problem of catalysis. However, it would be illogical to claim that all catalytic processes have an ionic mechanism. Surely in many cases simple dissociation of molecules, requiring much less energy than ionization, will be deemed sufficient activation, to explain the catalytic behavior of many surfaces. However, the possibility of ionic mechanisms of catalytic processes must be kept in mind, since the present experiments show that at least some molecules adsorbed on surfaces are in an electrically charged condition.

Ozone formation. Since ozone is readily produced in an ozonizer under the influence of ions it might be supposed that this substance upon decomposition should produce ionization. This idea was indeed held by several investigators and was especially favored at one time. The conductivity of air or oxygen passing over phosphorus was thought to be caused by the decomposition of ozone. Schenck, Mihr and Banthien (48) tested this point and showed that ozone has no electrical conductivity during decomposition or during an oxidation carried out by its use. Earlier investigators, for example Uhrig (69) and Richarz (70), as well as later workers as Ruyssen (71), Pinkus and co-workers (72, 73) and Brewer (74), find small ion currents during the thermal decomposition of ozone. But Hellmann (75) could not detect conductivity in the decomposing gas even though he expected to be able to find one ion per 5×10^{15} molecules decomposing. The other investigators find this ratio to be of small value (10^{-11}) in any case. Whether or not ionization accompanies the thermal decomposition of ozone can perhaps be best decided when other reactions which have been studied are reported.

Other gas reactions. The oxidation of nitric oxide:

$$2NO + O_2 \rightarrow 2NO_2$$

has been studied by Pinkus (76), who earlier reported no ionization but in his later work (77) joins with Reboul (31), Brewer and Daniels (78), Brewer (74) and Henry (79), who find a small amount of ionization during the oxidation carried out in a field. The chlorination of nitric oxide yields ions when chlorine is in excess:

$$2NO + Cl_2 \rightarrow 2NOCl$$

according to Pinkus (72, 76), but no ionization was found by Trautz and Henglein (80). Nor can these investigators find ion formation with the reactions:

$$2NO+Br_2 \rightarrow 2NOBr;\ 2HBr+Cl_2 \rightarrow 2HCl+Br_2;\ H_2+Cl_2 \rightarrow 2HCl$$

Pinkus (81) criticizes their work and suggests that ionization is greatest at the moment of mixing and first reaction, but dies out rapidly thereafter. If this were so, frictional effects might be held responsible for the phenomenon. Pinkus and de Schulthess (72) find ionization with the following reactions involving ozone:

$$2NO + O_3 \rightarrow N_2O_5;\ 2NO_2 + O_3 \rightarrow N_2O_5 + O_2$$

Brewer (74) studied the first reaction and found conductivity as well in the reactions:

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2;\ 2NO_2 \rightarrow 2NO + O_2$$

This investigator also studied (82) (Fig. 77) the oxidation of a variety of vapors and found a small conductivity when the reactions were carried out at somewhat elevated temperature (650° K.) between gold electrodes to which an electric field was applied. The gases studied were ethyl alcohol, xylene, toluene, benzene, acetone, normal butyl alcohol, normal propyl alcohol, gasoline, hexane, ethyl ether, amyl ether and hydrogen.

In all these chemical changes studied the number of ions formed per molecule reacting is very small: about one charge is detected per 10^{12} molecules undergoing chemical change. It is this great difference which leads to the view that most probably the ions formed are not concerned with the main mechanism by which the reaction proceeds. However, the general picture discussed in connection with the reactions involving sodium-potassium alloys and the slow oxidation of phosphorus may well be applied to the reactions just outlined. Although usually the reaction goes via a mechanism whereby the energy evolved follows the more usual path and is given out as "heat of reaction," a few of the molecules of a large number may so interact that ionization results. The energy of reaction then accumulates on some of the reactants or products in such a way as to ionize them. Reactions accompanied by ionization would then be expected to be most likely possible with the alkali metals or very large molecules, for they have the lowest ionization potentials. On this view, it would be necessary to suppose that chemiluminescence should be found in many cases if means existed for the detection of very small intensities of radiation. In a photochemical experiment, Lazarev and Rodzevich (83) found ionization when certain organic dyes were suspended in a gaseous medium. When these dyes underwent photochemical reaction, negative charges appeared on the gas molecules. The charges depend on the nature of the gas. The effect is stronger in gases which cause fading of the dye.

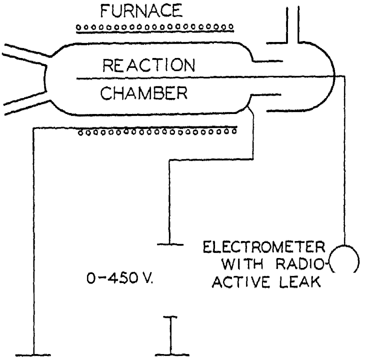

FIG. 77.—Reaction vessel and electrical connections for study of ion emission during chemical reaction. Brewer and Daniels, Trans. Am. Electrochem. Soc. 44, 259 (1923).

The view that contact catalysis may be due to ionization phenomena has been mentioned. Brewer (84) considers this mechanism in detail and proposes a theory of contact catalysis based on the following points. The ionization detected with every reaction is specific and is proportional to the number of reacting molecules. The ions liberated in a reaction originate on the surface of the electrodes, which serves as catalyst. A very high voltage would be required to obtain saturation, for the ions are held by strong forces which include the image forces due to their charge. The ionization current as well as the amount of chemical action are functions of the surface. An equation of the Richardson type for thermions is applicable to the chemical case as well. Nyrop (85) proposes a similar theory of contact catalysis.

However, it must be said again that other forms of activation such as dissociation will certainly have to be included in the whole complex of reaction possibilities on a catalytic surface. But the possibility of ion production during chemical action has been established.

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CHAPTER XIX

CATHODIC SPUTTERING OF METALS AND GAS DISAPPEARANCE IN DISCHARGE TUBES

Introduction. The phenomenon of sputtering of metallic cathodes has been observed by many investigators. It may be briefly described as follows: when a metal serves as a cathode in a luminous gas discharge it is found that the glass walls of the discharge tubes become covered with a layer of the metal as the tubes continue to operate. The metallic deposit on the glass walls may be of a variety of textures. At times beautiful mirrors may be produced, and again a more or less amorphous-looking deposit may result, depending on conditions. One can readily understand that it was recognized early that this phenomenon might be of value for the production of metallic mirrors, and there has resulted a definite technique for the production of smooth metallic surfaces, valuable as mirrors for optical instruments.

From the point of view of this monograph the phenomenon of cathodic sputtering is of interest because naturally the question arises as to the nature of the interaction between the ionized gas and the material of the electrode. Is this interaction a purely physical phenomenon, or does chemical interaction play a part? The question may be answered at once in the sense that the opinion of investigators favors the physical view of the interaction. Of course, if the gas present in the discharge can form chemical compounds with the electrode material, it is possible that chemical action will take place, but rather as a secondary phenomenon.

The early literature on the subject is quite extensive and has been summarized to 1912 by Kohlschütter (1) and to 1926 by Fischer (2). Seeliger discusses the topic as part of the phenomenon in discharge tubes (3). The earlier investigations established the following facts:

Cathode sputtering is observed usually in the luminous discharge, at gas pressures from a few thousandth to several millimeters of mercury and with currents of the order of several milliamperes. In a spark discharge there are indications of sputtering, and in an arc the cathode may become so hot that its evaporation is a prominent feature and then the phenomena in the arc cannot be compared with those where sputtering is usually observed. The type of discharge commonly adopted and best fitted to obtain sputtering is one showing a negative glow, where there exist a cathode drop of several hundred volts, a Faraday dark space and a positive column. The gas pressure has only a secondary influence. It affects the cathode drop which depends on gas pressure. The voltage drop near the cathode is of great importance; it appears that the amount of sputtering is proportional to the cathode drop at least above a threshold value. There also seems to exist a maximum voltage above which the weight losses of the cathode are no longer directly proportional to the cathode drop and where the whole phenomenon becomes very irregular in nature. This limiting value also depends on the gas used in the discharge tube. It would be expected that the form and shape of the discharge tube might exert some influence upon the sputtering process but only because the detailed electrical conditions in a luminous discharge are dependent upon the nearness of the glass walls to the electrodes. The earlier investigators were not certain regarding a possible influence of an electrical field on the sputtering process, although some observations seemed to indicate an effect. Similarly a magnetic field appeared to have a slight influence under some conditions (4, 5). The temperature of the cathode has no influence, and the sputtering process cannot be considered to be a general evaporation of the cathode.

As the various metals differ greatly in their ability to sputter, the idea originated early of arranging them into a sputtering series. The attempt to correlate this series to other properties of the metals was not successful. A type of Faraday law similar to the well-known laws of electrolysis in solutions was considered but could not be established with any rigor. Barring chemical action, the heavier gases are more efficient in producing sputtering of metals. Even aluminum electrodes which do not sputter easily are affected to a considerable extent by the heavier rare gases. Protecting layers such as oxide skins may stop the cathodic disintegration or at least produce a period of induction during which the protecting layer is removed, whereupon the sputtering process will proceed.

One of the earlier ideas for an explanation of the sputtering phenomenon involved the disruption of the cathode by occluded gases which were supposed to be liberated under the ion bombardment. There is no doubt that occluded gases may cause the disintegration of a cathode by their expansion and consequent removal of small crystals. However, since uniform sputtering can be produced with cathodes at red heat, where gas occlusion must be small, the presence of absorbed gases cannot account for the phenomenon as a whole.

During sputtering the gas pressure can both increase and decrease. Increased gas pressure must be due to liberation of absorbed gas and chemical decomposition of composite layers (oxides), and gas disappearance is caused by the occlusion of gas in the sputtered metal layer formed on the walls of the discharge tube. Another reason for decrease in gas pressure may be the removal of gas by chemical combination ,with the metal of the cathode or any other reactive material in the vicinity of the reaction zone. Since rare gases disappear as readily as more chemically reactive ones, one would incline towards the view that physical adsorption is the reason for gas disappearance.

It was found that canal rays, which were studied after their passage through an orifice in the cathode, also produced sputtering in much the same manner as they did upon the cathode proper. Since these canal rays were known to cause a variety of chemical changes on cathodes which were made from composite materials, such as sulphides for example, it was natural to consider the possibility of chemical action in relation to the sputtering phenomenon.

As far as theoretical views are concerned it can be said that most of the earlier investigators did not consider the phenomenon to be one of general evaporation of the cathode due to the heating of the *whole* electrode by the impinging positive ions. However, the *local* heating of the metal at the point of impact and the local evaporation of the electrode were considered, and thus a thermal view was adopted. Another, more indefinite, view ascribed the phenomenon to an increase in the evaporation under the electrical forces acting on the metal. A definitely chemical theory was considered. On this basis the impinging gas atoms were thought to form transient chemical compounds with the metal which, on leaving the cathode, deposited on the tube walls and there completely or partially decomposed. The fact that rare gases were useful agents in the sputtering process was not altogether proof against the chemical theory, for the ionized rare gases may show different chemical properties from the neutral structures we ordinarily deal with.

However the physical theory of ion-impact and consequent emission of secondary atom rays from the electrode seems to be the most satisfactory picture of the process. The number of emitted atoms will increase with the number of impinging ions and will therefore be proportional to the current, and, at constant current, the number of emitted atoms will be expected to increase with the energy of the impinging ion and hence will be proportional to the cathode drop. For given conditions of current and cathode drop the amount of sputtering will depend upon the metal of the cathode, because the work of removal of various metal atoms will be different and the separate gases may act individually in regard to their ability of transferring energy to the electrode.

The remarks made so far give the situation as summarized by Kohlschütter (1). As already mentioned, Fischer (2) dealt with the subject in a later article and distinguished more clearly between several phenomena of a similar nature. He discusses two types of sputtering: mechanical-thermal and electrical-impact sputtering. It is clear that a hot wire free from gas contained in a thoroughly evacuated bulb can evaporate only because of the fact that all materials have some vapor pressure, at any temperature. The evaporated material will leave the metal as atoms. If, however, the metal contains traces of gas we can expect a faster disintegration of the electrode with a greater amount of occluded gases. This last-mentioned phenomenon is called thermal sputtering, and the metal will leave the surface in larger pieces of even microscopic size. Evaporation and thermal sputtering may be reduced by the presence of a gas which is chemically inactive. Chemically active gases may have a varied influence upon the two phenomena just mentioned.

However, the observations usually classed under the term sputtering are all made in the presence of an electric field with the metal suffering disintegration negatively charged. If the metal is the anode, usually negative electrons only bombard it and very slight sputtering is noted. Cathode sputtering, electrical sputtering or electrical impact sputtering is produced by the impact of positive ions upon a metal cathode. With thin cathodes it has been observed that the insulating glass or quartz support may show disintegration due to the bombardment suffered as studied by Waran (6).

The sputtering of thorium. In most of the earlier work on the sputtering of metals, the conditions under which the experiments were carried out are not as satisfactory as might be desired. This situation is, of course, due partly to the fact that the various techniques involved had not been worked out. In many instances the amount of sputtering could not be determined with any accuracy. It therefore seems proper to discuss an example in more detail where the number of sputtered atoms could be measured with very great precision, as in the removal of thorium atoms from a thoriated tungsten wire as studied by Kingdon and Langmuir (7–9). It is a well-known fact that a tungsten wire covered with a monatomic layer of thorium has an immensely greater emission (10^5 fold at 1500° K.) than pure tungsten under the same conditions. The disappearance of thorium atoms due to a sputtering gas could therefore be detected with extraordinary ease by merely measuring the emission of thoriated tungsten before and after the sputtering process.

The effect of the gases argon, cesium, helium, hydrogen, neon and mercury at a pressure of six bars was studied as a function of voltage and pressure. Hydrogen ions produced no sputtering of thorium up to 600 volts energy. Argon, cesium, mercury and neon ions initiate the sputtering process at about 50 volts, and when these ions have 150 volts energy then it requires 12.5, 12.0, 23 and 45 such ions respectively to remove 1 thorium atom from the surface. Although helium does sputter at about 35 volts, this ion is very inefficient since it requires 7000 helium ions of 150 volts energy to dislodge 1 thorium atom. However, the sputtering in the special case of thorium is not generally found to be proportional to the energy of the impinging gas ions as has been noted in so many earlier investigations on other metals even though a threshold value seems to exist.

Kingdon and Langmuir develop a theory of sputtering to explain the rate of deactivation of the thoriated filaments and the threshold value noted above. One might expect that a fully thoriated surface, upon bombardment by gas ions, would lose its emissive power rapidly and then more slowly as more tungsten surface became uncovered. Instead, the actual observation indicated an initial lag after which the rate of deactivation reached a constant maximum value and then decreased as the tungsten surface was approached. It appears that the first result of the bombardment by the gas ions is a penetration of the thorium atoms into the tungsten surface. A large number of depressions of atomic size are thereby created. After a time another gas ion will impinge upon the atoms located in the depressions and will be reflected by the thorium atoms located there. If we can assume that the impact just mentioned is nearly elastic, the gas ion may still possess enough energy to dislodge a thorium atom from the edge of the depression. This picture accounts for the initial lag in sputtering, mentioned above. It is suggested then that the removal of thorium atoms takes place at the edges of holes or depressions in the thorium coating. This theory also explains the initial voltage needed to produce sputtering in the case of some of the ions mentioned above. An application of the laws of conservation of energy and momentum to the processes involved gives the results shown in Table 27. It should be pointed out that the gas ion stream is most probably not of uniform energy since not all ions fall through the full potential V.

$$E = \frac{4eV}{300} m_c m_g \times \left\{ \frac{m_g - m_c}{(m_g + m_c)^2} \right\}^2$$

TABLE 27

SPUTTERING OF THORIUM ON TUNGSTEN

K. H. Kingdon and I. Langmuir, Phys. Rev. **22**, 148 (1923)

Gas ion	Threshold voltage for sputtering		Number of thorium atoms sputtered per ion of 150 volts energy
	Observed	Calculated	
H.............	>600	527	0.000
Ne............	45	40	.023
A.............	47	35	.080
Cs............	52	129	.084
Hg............	55	1600	.044
He............	35	142	.00015

E = energy of the cathode atom, received from the impact; V = voltage through which the gas ion has fallen; $e = 4.774 \times 10^{-10}$ e.s.u.; m_c = mass of cathode atom; m_g = mass of gas ion.

In order that the cathode atom may escape from the surface, its energy E must be equal to or greater than the atomic heat of vaporization. In the case of thorium on tungsten it is 203 k-cal. per mole or 8.8 e.v. For the case of neon atoms on a thoriated tungsten cathode

$$E \quad 0.22\frac{eV}{300} \quad \text{whence} \quad 300 \quad \frac{8.8e}{300} \quad \text{or} \quad V_0 = 40 \text{ volts}$$

From Table 27 it is seen that not all the observations can be accounted for satisfactorily on this theory. The values of the threshold voltage for mercury and cesium are much too high. This discrepancy may be due to the fact that the masses of these two ions are comparable in magnitude to the masses of the thorium atoms, the latter being driven far into the surface by the first impact and the second collision being then an interaction between a gas ion and a solid wall. The ion would therefore be able to keep more of its energy and remove thorium atoms at a lower voltage. Hull and Winter (10) state that ions of more than 25 volts energy can remove thorium atoms from a tungsten wire.

Observations indicate that the helium ion interacts differently from the others studied. Relatively large quantities of helium gas penetrated into the filament and could be recovered later by proper heat treatment. Since the theory just presented does not seem to apply to helium, Kingdon and Langmuir consider an earlier theory by Thomson (11) which involved a radiation mechanism. He suggested that the gas ions upon deceleration near the electrode produce radiation, which is absorbed in turn by the metal atoms causing their expulsion from the metal.

The case of thorium sputtering just cited is one of the most satisfactory investigations in this field. The discrepancies between theory and experiment indicate the very complex nature of the phenomenon under discussion. Gehrts (12) studied these experiments and suggests a somewhat different picture: Instead of supposing that the first ion striking the surface produces a depression by driving a thorium atom into the surface, he believes that the first gas ion hitting a thorium atom causes the latter's union with a tungsten atom of the surface to form an energy-rich surface molecule which suffers a further impact by a second gas ion, bringing about the decomposition of the complex and the removal of the thorium from the surface. The thermal theory to be discussed later (page 414) is thought insufficient to explain this important case of sputtering.

The cathodic disintegration of tungsten. In the research just mentioned, the tungsten wire serving as a support for the thorium must have suffered sputtering, but it was not possible to study this case by the method used. However, tungsten sputtering was made the problem of a special research by the staff of the General Electric Company, London (13). The progress of the disintegration was followed by measuring the change in resistance of the wire due to its loss of weight. The vessel used was a triode, the wire serving as the grid. Since it was made negative towards the heated cathode it would receive positive ions from the gas contained in the vessel. The gas was ionized by a field applied between a hot filament furnishing electrons and a nickel anode.

It was shown that the disintegration was independent of the temperature to about 1200° C. It increased regularly with the energy of the positive ions and is appreciable when its value does not exceed greatly that required to ionize the gas. There is no irregularity near the normal cathode fall. The disintegration in different gases increases in the order hydrogen, helium, nitrogen, neon, mercury and argon, indicating an increase with mass.

It should be pointed out that the accuracy claimed for these researches by the authors has been questioned by Fischer (2). Also, as in the case of thorium sputtered from tungsten, the positive ions do not have uniform energy since they may be produced anywhere in the field. But if the pressure of the gas is so low that the mean free path of the ions is greater than the dimensions of the vessel, the relation of their speed to the nature of the gas and the conditions of the discharge will be comparatively simple and probably much simpler than when the ions travel through the abnormal cathode fall as in an ordinary discharge. At low enough pressure it may be expected that the mean energy of the ions reaching the grid should be independent of the pressure and nature of the gas and of the thermionic current which produces the gas ions in the first place. Under the above-mentioned conditions, the disintegration of the wire should be independent of gas pressure and thermionic current if it only depends on the number and energy of the positive ions. The sputtering S expressed as the number of tungsten atoms lost per positive ion striking the grid, however, should be a function of the applied voltage V_0 and of the nature of the gas. The relation between the actual energy of the ions and the applied voltage is not determined, and therefore the ion energy is not known. At a pressure below 0.03 mm. Hg in neon-helium mixtures with an applied potential of 300 volts the sputtering S was found independent of the pressure. Similar results were obtained in other gases.

It was shown that the tungsten wire had to be bombarded by positive ions in order that sputtering may result. When the grid was made positive and hence served as the anode no disintegration could be observed. The sputtering can be expressed by the relation

$$S = a(V_0 - V_0')$$

showing that it is proportional to the applied voltage and that a threshold value V_0' exists. The results obtained in two different vessels are collected in Table 28.

TABLE 28

THE SPUTTERING OF TUNGSTEN IN VARIOUS GASES

Research Staff G. E. Co., London, Phil. Mag. **45**, 98 (1923)

Gas	V_0' Threshold voltage		S Number of tungsten atoms sputtered per ion with 150 volts applied	
	Tube I	Tube II	Tube I	Tube II
H_2	......	......	0.000	
He	......	......	.000	0.000
N_2	120	......	.020	
$\frac{3}{4}$Ne, $\frac{1}{4}$He	85	0	.060	.040
Hg	130	50	.025	.060
A	80	30	.100	.090

Since the peculiarly great ability of the rare gases to cause sputtering when very pure is greatly reduced by the admixture of some of the common gases, the research staff included in their investigations some mixtures of gases. However, these findings did not agree with the observations just mentioned. The effects observed were obtained in a different type of discharge from the usual luminous one, and therein may lie the difference in behavior of mixtures of gases.

The sputtering of thorium and tungsten was investigated under conditions which when further developed will yield the most satisfactory results regarding this interesting phenomenon. It should be mentioned that Oliphant (14) has studied the bombardment of metal surfaces with positive alkali metal ions from a Kunsman filament (15). He finds that positive ions can penetrate and break up a surface of metal without removing any of its mass. This action would most probably change the resistance of the wire, so that the method of the Research Staff may be inherently inaccurate in some instances. However, most observations have been carried out in the self-sustained luminous discharge, and some of these investigations will be discussed below.

Chemical and physical sputtering. The possibility that the sputtering process might be a chemical phenomenon was mentioned earlier, and Güntherschulze (16) has actually found cases of sputtering which are due to the definite chemical interaction of the sputtered metal and the gas carrying the discharge. The cases discovered by him concern the elements carbon, selenium, tellurium, arsenic, antimony and bismuth. The first five are known to form definite hydrides, and bismuth also shows a slight tendency towards hydride formation, although its hydride is not very stable. The sputtering process of these elements in hydrogen differs from the process taking place with other metals in the same gas. The difference in behavior is the following: (1) In the case of *physical* or *normal* sputtering, at pressures of about 1 mm. Hg, the metals deposit on the vessel walls very near to the disintegrating cathode. In the electrochemical case the region on the glass walls in the vicinity of the cathode remains perfectly clear. (2) In the normal case it is found that the sputtering increases as the anode-cathode distance is lessened, whereas in the chemical case the sputtering is practically independent of this distance. (3) The amount of metal removed from the cathode is a linear function of the cathode drop beyond the normal cathode fall in the case of normal sputtering; in the chemical case disintegration proceeds quite strongly at the normal cathode fall. (4) In the normal case metals sputter only when they serve as cathodes and they do not disintegrate as anodes, whereas in the chemical process the appropriate metals (As, Sb, Bi) will sputter even though they are not connected directly with either electrode of the discharge or whether they are cathode or anode. Hydrogen ions or atoms are evidently necessary for the chemical sputtering process. With increase in cathode drop the normal sputtering is added to the chemical disintegration and may even outrank the latter at sufficiently high voltage.

The sputtering obtained in hydrogen with twenty-four elements is shown in Table 29.

TABLE 29

CATHODE SPUTTERING IN HYDROGEN

A. Güntherschulze, Z. Physik **36**, 562 (1926)

Metal	Q mg. per amp-hr.	Q/A (A = At. wt.)	Metal	Q mg. per amp-hr.	Q/A (A = At. wt.)
W..........	57	0.31	Co..........	56	0.95
Mo..........	56	0.58	Fe..........	68	1.21
Cr..........	27	0.51	Au..........	460	2.34
Ta..........	16	0.09	Ag..........	740	6.8
Al..........	29	1.05	Cu..........	300	4.7
Mg..........	9	0.38	Bi..........	1470	7.0
Mn..........	38	0.69	Sb..........	89	7.4
C..........	262	22.	As..........	1100	15.3
Tl..........	1080	5.3	Te..........	(1200)	(9.4)
Pb..........	400	1.9	Cd..........	32	0.29
Sn..........	196	1.7	Zn..........	340	5.2
Ni..........	65	1.11			

The cathode was made from a large iron cylinder, 7 cm. in area and cooled by ice water. It carried a current of about 40 milliamp. at an applied voltage of 850 volts, which produced a cathode drop of 770 volts. The hydrogen pressure amounted to about 1 mm. Hg, and the duration of an experiment varied between 12 and 45 min.

It is seen that the metals, magnesium, tantalum and aluminum sputter least. This situation is usually explained by the assumption of oxide layers which protect these metals. Tungsten, molybdenum, chromium, manganese, cadmium and the metals of the iron group show a greater effect, and the other metals studied sputter quite readily. The metals carbon, arsenic, antimony, bismuth and tellurium which are sputtered by a chemical process show a clear space near the cathode which is about one and one-half times the cathode dark space. The disintegration in this case seems to be due to the chemical combination of the hydrogen ions with the metal atoms at the surface of the cathode. The hydrides formed diffuse into the gas phase and are there decomposed into the metals and hydrogen. The metals deposit on the nearest wall. In the region of the discharge represented by the clear space on the glass wall, the conditions for the decomposition of the compounds formed are not satisfactory, probably on account of lack of concentration of ions or electrons which cause the destruction of the hydride formed. Since the metal deposit is found on the glass walls even in the region of the anode it means that the metal is formed in all regions of the gas phase.

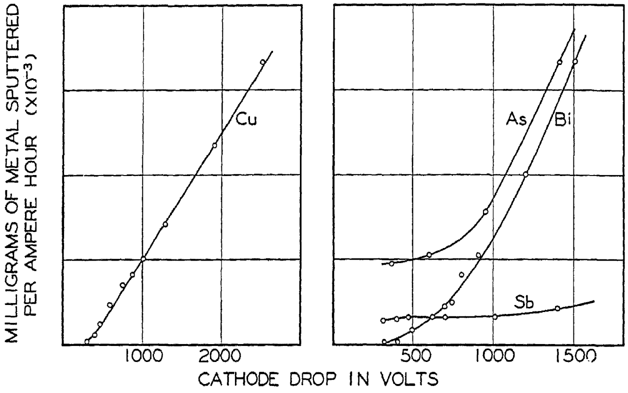

FIG. 78.—Physical sputtering (copper) and chemical sputtering (arsenic, antimony and bismuth) in hydrogen. Güntherschulze, Z. Physik 36, 563 (1926).

While the relation between the amount of sputtering and the cathode drop in the case of copper is a linear function above the normal cathode fall, the chemically disintegrated metals show an entirely different behavior. Even at the normal cathode drop they sputter readily and in the order: arsenic, antimony, bismuth, which is also the order of the stability of their hydrides. As is seen from Fig. 78, the sputtering at lower voltages does not rise linearly with the cathode drop, which must mean that it depends on the number but not on the energy of the hydrogen ions reaching the cathode. The process is a chemical reaction between the ions and the metal, and only at higher values of the cathode drop does proportionality of sputtering and voltage set in, showing that the usual physical process of disintegration has been added to the initial chemical one. As mentioned earlier, the chemically sputtered metals will disintegrate as cathodes, anodes or even when located in the discharge without electrical connection to the metal electrodes, indicating clearly the great difference between the chemical effect and the normal or physical sputtering process. Güntherschulze was further able to remove the already sputtered antimony from the wall by continued action of the discharge, showing that an increased amount of hydrogen ions or atoms is able to remove the deposit.

A further relation studied by Güntherschulze deserves mention, for it has a definite bearing on the modern view of the sputtering process. It is the dependence of sputtering on the cathode-anode distance. As has been stated above, the amount of disintegration increases as this distance is decreased. For larger distances of several millimeters there is no effect, but as the region between the electrodes decreases a very rapid rise is noted. It appears that even larger sputtering could be obtained were it possible to bring the electrodes still closer together. The largest sputtering is noted at the shortest distance, which, however, cannot be further decreased without changing the electrical conditions of the discharge. The largest sputtering values are the ones shown for copper in Fig. 78. These experiments illustrate that, under ordinary conditions where the cathode-anode distance is of appreciable magnitude, a great deal of sputtered metal must be constantly returning to the cathode. This is confirmed by the fact that many times the cathodes are covered with a fine metal dust which can readily be wiped off.

The laws of cathode sputtering. In another investigation Güntherschulze (17) showed that in the case of silver sputtered by hydrogen the following relation gave the dependence of the amount of sputtering on the variables of the problem:

$$V$$

where $Q_{\mathrm{Ag,H_2}}$ = the amount of the sputtered silver (milligrams per ampere-hour); c = the electrode distance (centimeters); p = the pressure of hydrogen (millimeters of mercury); V = the cathode drop (volts); $C_{\mathrm{Ag,H_2}}$ = a constant of proportionality = 0.868 for silver and hydrogen.

An improvement in the experimental conditions concerned the use of a guard ring so as to avoid the proximity of the glass walls. The arrangement which permitted this situation to be realized is shown in

Fig. 79. The fact that the quantity of sputtered metal is inversely proportional to the distance between cathode and anode suggests that the sputtered metal reaches the anode by a process of diffusion as a metallic vapor through the hydrogen. Since the estimated pressure of silver atoms was of the order of 10^{-4} mm. Hg in a hydrogen pressure of 0.72 mm. Hg. the silver atoms have little opportunity of making impacts and hence little chance of agglutination. They will therefore traverse the gas phase most probably as single atoms unless the cathode-anode distance is very large. Since the process of metal transfer appears to be one of diffusion it is probable that the silver atoms do not leave the cathode with energies much larger than the thermal energies of room temperature. The actual quantities of sputtered-metal are still a small fraction only of the amount of metal which diffuses back to the cathode. That this is so was shown by studying the disintegration of a fine wire when the sputtering is much larger, relatively speaking, because the back diffusion is practically eliminated on account of the small area exposed by the wire.

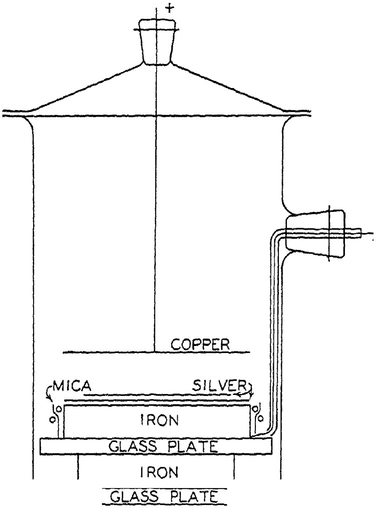

Fig. 79.—Sputtering apparatus with guard ring arrangement. Güntherschulze, Z. Physik **38**, 575 (1926).

The new result that the sputtering should be proportional to the cathode drop is much easier to understand, whereas the older formula

$$Q = C(V - V_0)$$

had always been unsatisfactory, for it was difficult to comprehend why the sputtering should be zero at the normal cathode fall, where after all the impinging hydrogen ions must possess considerable energy.

Charge on sputtered metal. It has been inferred above that silver sputtered by hydrogen leaves the cathode in the atomic condition, because the process appeared to be one of diffusion of a vapor through a gas. Definite evidence that the sputtered metal leaves the electrode as a stream of atoms has been obtained by v. Hippel (18). He showed that the greatest portion of such metals as cadmium, zinc and silver gave their atomic spectra in the neighborhood of the cathode, and he developed a spectrographic method for the measurement of vapor pressure by comparing mercury and metal resonance lines. Baum (19) showed by direct observation in a magnetic field that silver sputtered in hydrogen leaves the cathode as atoms, although they may later acquire a positive or negative charge. Sommermeyer (20) studied the transport to the anode of metal sputtered at the cathode. At high sputtering rates in rare gases it appears that a good deal of the material follows the lines of force, i.e., behaves as if charged negatively. He could not decide whether negative atoms or mole ions on the one hand, or large particles on the other, were responsible for the transport observed.

Measurement of the metal deposit. A further careful investigation of the sputtering of various metals was carried out by Blechschmidt (21). He preferred the determination of the amount of metal deposited upon a glass plate, rather than the more usual method of determining the weight loss of the cathode by direct weighing. Two reasons for this preference are: First, the presence of oxide skins or layers of absorbed gases or other impurities cause the existence of a period of induction in the sputtering process during which the disintegration does not proceed smoothly. The current passing during this induction period should not be counted in the electrical quantity responsible for the amount of metal sputtered. It is easy to cover the receiving glass plate during this initial period. Second, it has been found that a large amount of the metal returns to the cathode, and this portion is not included in the weighing method. Blechschmidt established the following facts: (1) The metal deposit is directly proportional to the time of sputtering after the initial period mentioned above. (2) The deposit depends on the cathode-anode distance. Beyond the cathode dark space there exists apparently an exponential decrease with increased distance. A glass plate placed in the dark space protects the cathode from the impact of the canal rays like an object in a light beam. (3) No dependence on temperature was noted as long as the gas temperature was not affected by the processes taking place at the cathode. (4) The intensity of sputtering is not proportional to the voltage. The curve "intensity vs. voltage" reaches the voltage axis asymptotically, and it does not cut the axis at the normal cathode fall. A lower or upper limiting value has not been observed. (5) A part of the metal returns to the cathode. (6) The metals sputter in the following sequence:

Hydrogen: Pb, Sb, Ag, Au, Bi, Cu, Pt, Ni, Fe, Cd.

Nitrogen: Ag, Au, Sb, Pb, Bi, Cu, Sn, Pt, Ni, Cd, Fe, W, Zn.

Argon: Cd, Ag, Pb, Au, Sb, Bi, Sn, Cu, Pt, Ni, Fe, W, Zn, Al, Mg.

(7) The intensity of sputtering increases with increase in the atomic weight of the gases mentioned. (8) Several of the metals show chemical effects. (9) Ignoble metals show permanent or temporary decreased sputtering.

The thermal theory of cathodic sputtering. On the basis of the extensive experiments by Blechschmidt (21), v. Hippel (22, 30) discussed the thermal theory of sputtering. Waran (23) adopted the same views, and Cowsik (24) furnished additional evidence. Morgulis (25) considered the sputtering phenomenon an emission of electrons and atoms. The fundamental notion is the idea that the metal cathode shows local evaporation at the points of impact of the positive ions. v. Hippel also measured their energy by permitting some of them to pass through a small orifice in the cathode and determining their energy by appropriate retarding fields. The impinging ions show a considerable spread in velocity from zero volts to values nearing the cathode drop. Baum (19) found silver atoms sputtered by hydrogen to have a velocity of 570 meters per second. The average velocity of silver atoms evaporated at the melting point of silver (961° C.) is 534 meters per second. The evaporation of *atoms* sets in as soon as the ion has struck and dies out rapidly as the available energy of the ion, made up from its ionization energy and the kinetic energy obtained from the field, has been used up.

The final relation obtained by v. Hippel (30) for the intensity of sputtering is

$$I = B \times \frac{i}{1 + C_e} \times \left\{1 - r(\overline{T})\right\} U_1 \times \frac{3nk}{\kappa b} \times v_m \times e^{-[q+W_1(\overline{T})]/kT}$$

where I = the total number of sputtered atoms leaving unit area of the cathode per second.

B = proportionality constant.

$\frac{i}{1 + C_e}$ = the number of positive ions reaching unit area of the cathode per second.

C_e = number of secondary electrons liberated per positive ion impact.

i = current.

$\bar{T}$ = average temperature of the impact spot.
$r(\bar{T})$ = reflection coefficient for positive ions.
U_1 = energy in the form of heat released at the cathode per positive ion.

$B \times \frac{i}{1 + C_e} \times \{1 - r(\bar{T})\} U_1$ = number of atoms able to sublime.

$_{\kappa b} \times \nu_m \times e^{-[q+W_1(\bar{T})]/kT}$ = probability factor depending on speed of evaporation and heat conductivity stating how many atoms really will leave the cathode.

n = atom surrounding the one ready to sublime.
k = Boltzmann constant.
κ = atomic heat conductivity.
b = interatomic distance in the metal.
ν_m = period of vibration of atoms in the metal.
q = atomic heat of sublimation.
$W_1(\bar{T})$ = work function of atoms on cathode surface.
T = cathode temperature.

The sublimed metal will leave the cathode by diffusion through the gas of the discharge. These ideas seem to serve as a satisfactory basis for the considerations of the sputtering phenomenon. It should be pointed out that the scattered metal quantity is often referred to the total quantity of electricity passed. Since no separation of current carried by the positive ions and electrons has usually been made, the total current is used in such calculations. This situation may at times vitiate the calculated intensity. v. Hippel points out again the difficulties that may arise from oxide layers and from direct chemical reaction between the activated (ionized) gas and the metal. Roughly, it is found that the intensity of sputtering increases with the heat of sublimation of the metals.

It must always be kept in mind, however, that secondary processes will disturb the simple picture of local sublimation just outlined. The cathode is affected as a whole in the sense that regular etching figures can be produced as Baum (19) has shown. Furthermore, under prolonged sputtering the electrode can superficially melt. It is necessary to furnish ample cooling to avoid such difficulties.

Metastable atoms. Some evidence which would indicate that the sputtering process is not altogether a simple local evaporation, but that the charged nature of the impinging ions has a definite influence, is given by Oliphant (26). He has shown that though metastable helium atoms will cause sputtering they are not as efficient as ions of the same kinetic energy. He found that the heating effect of metastable atoms is of the same order of magnitude as that produced by positive ions, hence they possess the same kinetic energy when reaching the electrode. But their ability to sputter was distinctly less than the effect of helium ions.

Impact and evaporation theory. The two theories mentioned so far which seem to deserve consideration may be called the impact theory of Kingdon and Langmuir and the local evaporation theory of v. Hippel. In the first, the momentum of the impinging ion is transferred to the metal atom and one might expect some relation to exist between the direction of motion of the two interacting particles. On the evaporation theory, however, the locally evaporated metal should volatilize in all directions with equal probability and should follow the cosine law. This question of direction of evaporation has been studied by Seeliger and Sommermeyer (27). They arranged a beam of canal rays produced in a discharge of argon of 5000–10,000 volts and caused them to impinge upon a liquid surface of gallium and also upon a silver strip. The final arrangement is shown in Fig. 80. The uniform deposit obtained shows that the cosine law holds for the sputtering process. Since it also holds for the case of thermal evaporation as has been shown by Knudsen (28), these experiments indicate that sputtering is a process of evaporation. The canal rays exercise no directive influence on the sputtered atoms. So far this situation has been shown to be true only for ions of large energy.

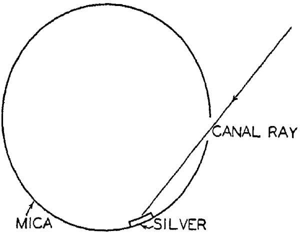

Fig. 80.—Apparatus used to test the cosine law of reflection for sputtered silver atoms. Seeliger and Sommermeyer, Z. Physik 93, 692 (1935).

Effect of cathode temperature. The earlier investigators Kohlschütter (1) and also Kingdon and Langmuir (9), the Research Staff of the General Electric Company (13) and Blechschmidt (21) found no dependence of sputtering on cathode temperature. However, Ingersoll and Sohrdahl (29) reported an increase in sputtering of gold, nickel and platinum in argon near 1000° C. But this increase is not so rapid as the vapor-pressure rise with temperature. The temperature effect depends on the gas. The sputtering of nickel in hydrogen is not increased so greatly as the sputtering in argon.

The effect of oxide layers. In a special investigation Blechschmidt and v. Hippel (30) showed that removal of the oxide coating produces metal surfaces which sputter normally. They formed their cathodes by evaporation in a vacuum. Such surfaces are clean and show the expected sputtering. The metals investigated were cadmium, zinc, antimony, bismuth, lead and magnesium in a helium-neon gas mixture which was continually purified by pumping through activated charcoal. The results appear to fit the thermal theory of sputtering in the sense that the sputtering intensity follows the heats of sublimation of the metals.

That aluminum and even beryllium can be sputtered if the oxide layer is removed has been shown in a special research by Kueck and Brewer (31). They destroyed the initial oxide layer by continued sputtering in helium. After the electrodes were clean they obtained sputtering in pure helium (0.5 mm. Hg) with a current of 10 milliamp. In 15 min. thin transparent films of the metals were deposited on the walls of the tube.

Oliphant (14) studied the sputtering of metals by positive alkali ions from a Kunsman source (15) and noticed a certain voltage below which the positive ions are unable to penetrate the gas layer covering the metal. This critical voltage varies with the gas. It is 530 volts for oxygen, 400 volts for nitrogen and 300 volts for argon. At higher voltages the alkali ions can penetrate the adsorbed gas layer and attack the underlying metal. With thoroughly outgassed targets no definite voltage could be determined below which the metal was not attacked. This effect with outgassed targets was only of the nature of a discoloration and roughening of the surface. With thoroughly outgassed metals the actual sputtering seems to be less. The presence of a little gas facilitates the removal of the metal.

Very low gas pressures. Since the gas pressures usually employed in gas discharge tubes range from about one half to several millimeters of mercury and since under these conditions the back diffusion of sputtered metal must be very large, Güntherschulze and Meyer (32) studied the sputtering process at such low gas pressures that most of the sputtered metal had a chance to leave the cathode. For this purpose they investigated the sputtering of silver and copper in argon, nitrogen, neon, hydrogen and helium at 1200 volts. In order to realize the desired conditions they employed a heavy discharge of 3 amp. from a filament and took out of the body of the discharge positive ions which reached a Langmuir probe on which surface the sputtering was observed. It was found that in argon the sputtering was independent of the pressure below 0.01 mm. Hg, showing that under this pressure all metal atoms removed from the probe also left it. Pure helium showed no sputtering up to 800 volts, but a large amount of gas was removed during the action of the discharge. Other gases were similarly absorbed. In order to estimate the efficiency of the sputtering process Güntherschulze (33) determined the energy carried to the Langmuir cathode by the cations alone. Upon comparison with the heat of sublimation it is found that the process of sputtering is a very inefficient one as far as use of gas-ion impact energy is concerned. For example, it took 442 × 10^3 watt-sec. to sputter 1 gram of copper. Since the heat of evaporation of copper is 4.66 × 10^3 watt-sec. per gram, the efficiency is only 1.05%.

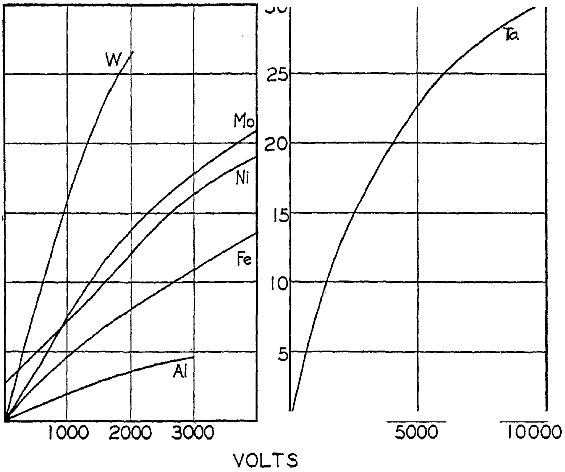

FIG. 81.—Sputtering of metals in mercury vapor (1.1 × 10^3 mm. Hg). Current about 1 milliamp. Meyer and Güntherschulze, Z. Physik 71, 279 (1931).

These experiments at low gas pressure were continued by Meyer and Güntherschulze (34) to include mercury vapor in order to discover how the sputtering would proceed when the impinging ion was considerably heavier than the metal atoms to be dislodged. The metals studied were: Be, Al, Si, Cr, Mn, Fe, Co, Ni, Cu, Zr, Mo, Pd, Ag, Ta, W and Pt. At mercury pressures less than 0.005 mm. Hg the amount of sputtering was found to be independent of the pressure. Again a Langmuir probe was used up to 10,000 volts. The relation between amount of metal removed per ampere-hour (Q/Ih) and the sputtering voltage is shown in Fig. 81. It is seen that at lower voltages there is proportionality between sputtering and voltage, but that the slope for tantalum at 1000 volts is 0.008, and only one-tenth of this amount at 10,000 volts.

Since the process of sputtering is thought to be a local vaporization, one would expect that the quantity Q/Ih might be proportional to the heat of sublimation. The appropriate data are given in Table 30.

TABLE 30

Sputtering of Various Metals in Mercury Vapor

K. Meyer and A. Güntherschulze, Z. Physik **71**, 279 (1931)

Metal	Q Metal sputtered, grams per ampere-hour	A Atomic Weight	Q/A Number gram atoms sputtered per ampere-hour $\times 10^3$	Heat of evaporation, kilocalories per gram atom
Al.	1.07	26.97	39.7	48
Si.	1.12	28.06	39.8	44
Mn.	2.25	54.93	40.9	
Fe.	2.31	55.84	41.4	113
Ni.	2.40	58.69	40.9	
Zr.	3.39	91.22	37.2	
Mo.	3.92	96.0	40.9	177
Ta.	7.40	181.36	40.8	
W.	7.65	184.0	41.6	218
		Average.	40.36	
Be.	0.428	9.02	47.5	
Co.	3.44	58.97	58.4	
Cr.	3.49	52.01	67.1	
Cu.	6.89	63.57	108.0	50.8
Pd.	10.42	106.7	97.5	45
Pt.	15.76	195.2	80.7	127
Ag.	20.47	107.88	190.0	45

It is found that the number of metal atoms sputtered per mercury ion hitting the surface shows no relation to the ordinary heat of evaporation. On the other hand the remarkable fact comes to light that for the first nine metals given in Table 30 the number of atoms removed per mercury ion is the same! These nine metals do not amalgamate readily with mercury, while the last seven metals mentioned are more prone to do so. In this last fact Güntherschulze sees the difference in the behavior of the two groups. The increase in the number of atoms removed in the second group of metals is due to the fact that the mercury residing on the surface will assist in the removal of metal atoms. However, the situation is not clear as yet, and further experiments must be performed before this interesting fact can be interpreted.

Alloys. It seems of some interest to investigate the sputtering of alloys in order to find out if the constituent metals of the alloy sputter independently or if their state in the matrix has an effect on their cathodic behavior. Several investigators have dealt with the question lately. Mazur (35) studied the metals tin, copper and tellurium and the alloys of aluminum and tin containing 25, 50 and 75% of the first metal; bismuth and cadmium containing 90.6% and 13.4% of bismuth; antimony and tin containing 30, 90 and 9% antimony; zinc and antimony with 51.3% of the first element; aluminum and copper alloys with 3 and 10.5% of aluminum; and a copper-tin alloy with 33 and 57.5% of the last-mentioned element. He sputtered these metals and alloys in hydrogen and obtained etch figures such as are formed by the use of acid. Metals which do not dissolve in the solid state sputter differently, and one can distinguish the constituents on the sputter-etched surface. In alloys which form chemical compounds, the latter act as units, as for example tin antimonide (SnSb). The composition of the sputtered metal is not the same as that of the original alloy. Belladen and Surra (36) also studied the cathode sputtering of zinc-copper alloys in hydrogen and in air. These show the same anomalous behavior as zinc. With low current and at low potential the quantity of metal pulverized diminishes with increase in the zinc content of the cathode. At higher potentials the alloys richest in zinc sputter the most. An increase in potential or current does not notably influence the composition of the sputtered metal. However, the percentage of copper was slightly higher in the alloys pulverized during the first stage of operation. Other alloys investigated by Belladen (37) are copper-nickel, cadmium-antimony and copper-antimony. The first pair is completely soluble in the solid state, and the last two sets form definite chemical compounds. In the case of copper-nickel alloys, for specimens poor in copper, the sputtering is found to be greater than calculated on the assumption that the two components behave in the alloy as in the pure state. Correspondingly the fraction of copper in the sputtered metal is greater than in the original mixture. In alloys containing more than 30% copper, the sputtering is less than the calculated value and the sputtered material contains relatively less copper. For cadmium-antimony alloys a maximum value for sputtering is found at a composition corresponding to the compound: CdSb. Samples containing more than 20% antimony sputter better than pure antimony, and the pulverized metal always contains more antimony. The maximum difference occurs with alloys containing 10–30% antimony. If the percentage of this component is increased, the composition of sputtered alloy approaches the original one. Copper-antimony alloys show a maximum of sputtering at 10% antimony, a minimum at 35% antimony, an increase from this composition to the composition given by the compound: Cu_2Sb. All alloys of these two metals sputter less than pure antimony. The sputtered metal contains more antimony than the original, and the difference increases up to the alloy containing 35% antimony. From alloys having the composition of the compound Cu_2Sb on, the sputtered and the original metal have nearly the same composition. Since hydrogen was used in some of these experiments it is clear that the component antimony sputters by chemical reaction.

Bismuth-antimony and copper-tin alloys were studied in a similar fashion by Belladen (37). The sputtering-composition relations in the first case resemble the behavior of copper-nickel alloys. The pulverized product contains more bismuth than does the original alloy if it contains less than 20% of this metal. In the case of copper-tin mixtures the compounds Cu_4Sn and Cu_3Sn appear to show special features in relation to sputtering. The varying behavior of these alloys in relation to sputtering can be understood on the modern views of crystal structure. An interesting point concerns the finding by Belladen that a deformed copper rod showed greatly decreased sputtering which on annealing increased to the customary value. Accordingly the phenomenon of cathodic sputtering may prove useful as a tool for the study of hardening and recrystallization.

An interesting experiment performed by Asada and Quasebarth (38) shows that the constituents of an alloy can be separated by the sputtering process. Copper foil containing a slight amount of gold will lose the gold on continued sputtering in mercury vapor and air. Pure gold sputters much more readily than copper, and it maintains this property in the alloy.

Chemical reactions during sputtering. We have seen that arsenic, antimony and carbon cathodes, for example, react with the excited gas and form hydrides which in turn decompose, depositing the respective metals on the walls of the tube (16). Similar studies were made by Berraz (39) on silver, gold and lead in nitrogen. The first two metals showed no interaction with the nitrogen of the discharge, but lead reacted to form an easily pulverizable deposit which gave ammonia with moist air:

$$Pb_3N_2 + 3H_2O \rightarrow 2NH_3 + 3PbO$$

The same author (40) found that copper would form cuprous nitride (Cu_3N) at pressures of 0.5 to 1 mm. Hg. The black iridescent deposit has properties similar to those of the nitride preparation obtained by ordinary chemical means. X-ray spectrograms were supposed to show that the deposit was crystalline and contained no excess metal.

Several other chemical reactions were studied by a group of Polish investigators and reported by Reczynski (41). He stresses the fact that atoms and molecules existing in a discharge are in excited and ionized states and hence must show different chemical properties from those exhibited by them in their normal condition. Since these gaseous ions receive considerable energy from the cathode drop they can make very close impacts with the atoms of the cathode conducive to chemical reaction. Furthermore the sputtered metal should be especially prone to react with the gas of the discharge because of its fine state of subdivision, and chemical and physical absorption should occur readily. Whether or not chemical reaction has taken place can be found out by the following means: (1) By spectroscopic analysis new lines and bands not belonging to the initial gas or the cathode metal can be discovered. (2) The quantity of gas adsorbed and the amount of metal sputtered can be used for the calculation of the relative amounts of substances consumed, provided of course that the total process is a chemical one. (3) The deposit on the glass walls can be analyzed. The reactions studied by the author and his co-workers are summarized in Table 31. The discharge used by these investigators is a low-voltage water-cooled arc at pressures of several millimeters of mercury.

With iron electrodes in nitrogen no absorption below 600 volts was noted, but at a higher voltage the absorption increased rapidly. The reason is that no disintegration takes place at the lower potentials; sputtering is necessary for absorption of gas and chemical reaction. The mere fact that excited nitrogen atoms and molecules are present in the discharge is not sufficient reason for nitride formation. In an arc with iron electrodes, in a mixture of nitrogen and mercury, the iron cathode is sputtered and forms nitrides, but the excited mercury atoms though present do not interact and no mercury nitride is formed, showing that the sputtering metals are prone to react. In the case of aluminum in nitrogen the nitride forms on the cathode at lower voltages but at high values a brown deposit forms on the wall. In the case of iron in nitrogen it was found that the amount of iron sputtered is equal to the amount of nitrogen disappearing in the ratio Fe: N, hence the probable formula of the nitride formed is FeN.

Increase of cathode temperature causes increased sputtering and gas adsorption. A tungsten filament heated by 20 watts with 200 volts applied shows a certain absorption of nitrogen. At 25 watts the same absorption can be reached with 100 volts; with 37 watts at 30 volts; and at 62 watts the absorption takes place, with no voltage applied at all, at a greater rate than in the three previous experiments. When a cathode of iron nitride deposited on a piece of glass is used, a very high cathode drop results and sputtering takes place without gas adsorption.

TABLE 31

CHEMICAL REACTIONS DURING SPUTTERING ACCORDING TO VARIOUS AUTHORS

Reactions	Remarks	Ref.
$2As + 3H_2 \rightarrow 2AsH_3$	No products isolated	(16)
$2Sb + 3H_2 \rightarrow 2SbH_3$	" " "	
$2Bi + 3H_2 \rightarrow 2BiH_3$ (?)	" " "	
$xC + yH_2 \rightarrow C_xH_{2y}$	" " "	
$Te + H_2 \rightarrow H_2Te$	" " "	
$Se + H_2 \rightarrow H_2Se$	" " "	
$3Pb + N_2 \rightarrow Pb_3N_2$	Deposit gave NH_3	(39, 40)
$3Cu + \frac{1}{2}N_2 \rightarrow Cu_3N$	Same as ordinary product	
$3Hg + \frac{1}{2}N_2 \rightarrow Hg_3N$	Product 93% Hg; 1.8% N_2; gold copper color; sublimes	(41)
$2Hg + H_2 \rightarrow 2HgH$	Band spectrum only; no deposit; Pressure lowered during run	
$3Zn + N_2 \rightarrow Zn_3N_2$	Deposit formed; it decomposes below 350° C.	
$2Zn + H_2 \rightarrow 2ZnH$	Band spectrum only; No gas adsorption	
$Zn + He \rightarrow Zn : He$ (??)	Gas adsorption during run; no spectrum	
$Zn + A$	No gas adsorption	
$Fe + \frac{1}{2}N_2 + (Hg) \rightarrow FeN + (Hg)$	Iron nitride forms deposit; Mercury does not	
$2Al + N_2 \rightarrow 2AlN$	Formed on cathode at low potential; at high potential it is removed to wall	

From these researches Reczynski concludes that chemical reaction will ensue when the reaction partners, i.e., cathode metal atoms and gas, have a sufficiently high relative kinetic energy. If there is a further excess the resulting compound molecule will vaporize and deposit on the wall. If the cathode is already a compound, sputtering but no gas adsorption takes place. Higher cathode temperatures are conducive to gas adsorption. The possible chemical reaction between metal and gas is the primary act, and sputtering and gas adsorption are secondary phenomena.

In other words Reczynski favors the older chemical theory of sputtering which was held very early by Kohlschütter (1). This theory necessitates the view that chemical compounds exist between metals and the rare gases and for this reason has not been favored. However, one must remember that the rare gases in excited states are by no means chemically unreactive.

Cathode loss in arc. Needless to say, the phenomenon of cathode sputtering will be intensified in the arc and moreover may well operate by a different mechanism. Uniform thermal evaporation may be involved more definitely than in the luminous discharge. Some preliminary measurements of iron, silver and copper in air and neon have been reported by Seeliger and Wulfhekel (42) and by v. Issendorff (43) on the losses of a mercury cathode in a mercury arc. Schmick and Seeliger (44) studied the transfer of matter in an iron arc. Most probably chemical sputtering will be prominent with the proper combination of metal and conducting gas.

Electrons. That electrons are very inefficient in producing anode sputtering has been shown by Bareiss (45) on barium and gold.

Technical uses of cathode sputtering. *Very thin metal films.* Lauch and Ruppert (46) have produced very thin metal films by sputtering onto highly polished sodium chloride crystals. The first step consists in sputtering a thick ring of metal while the center which will be occupied by the thin film is protected by a thin glass plate. After removal of the central glass plate the region is again sputtered. The underlying salt crystal is then dissolved in water. By this process they were able to produce silver foils of about 30-$\mu\mu$ thickness and 6-mm. diameter. Such films can withstand a pressure of 8 mm. Hg. These foils are uniform and free from holes and have a high metallic luster. The thinest sections made were only 5$\mu\mu$ thick and of 5-mm. diameter. Sheets 10$\mu\mu$ thick could have a diameter of 8 mm. Thicker foils of 40–50$\mu\mu$ could be prepared from silver, gold, platinum and nickel with a diameter of 3–4 cm. Similar films have been used by Thomson (47) for experiments on the diffraction of cathode rays.

He followed a method suggested by Joliot (48), who used a cellulose acetate support in the preparation of such films. Cold acetone will dissolve the support from the foils. He prepared sections of gold and platinum 10 mμ in thickness and 3 mm. in diameter.

A commercial method for sputtering gold electrode surfaces onto diaphragms of certain types of microphones is described by Fruth (49). Hulbert (50) developed a simple technique.

Reflecting metal mirrors. Cathode sputtering has been used for many years for the production of highly reflecting mirrors. These metal mirrors can be produced with the highest reflection coefficients suitable for astronomical and other optical instruments.

Cartwright (51) remarks that better mirrors are obtained when the glass is first heated to 200° C. in a vacuum before sputtering. The number of failures without obtaining a satisfactory one is greatly reduced by this process. It is very essential to have the glass surfaces clean. Since aluminum does not sputter easily, it can best be deposited as a mirror surface by evaporation (52).

Optical wedges. By an appropriate placing of the sputtering cathode to the receiving glass plate it is possible to produce films whose thickness will vary linearly from one edge of the glass plate to the other. If two metals are properly combined it is possible to produce optically gray wedges suitable for intensity measurements in radiation work, as suggested by Güntherschulze (53).

Preparation of alloys. He also suggests the preparation of alloys by sputtering two metals simultaneously from a cathode made up of the two metals in the shape of bars placed side by side. The sputtered material should then vary from one pure metal to the other, and all intermediate compositions should be attainable. Various physical properties, such as color, reflection and crystal structure, can be studied as a function of composition.

Etching of metals and alloys. Baum (19) and Mazur (35) produced etch figures by sputtering the specimens, and Smyth (54) obtained results with a very simple apparatus on copper-silver alloy. In some cases satisfactory etching was produced in 15 sec. (copper-silver eutectic); other alloys (copper-zinc) took longer. Smyth's apparatus is shown in Fig. 82.

Very high resistances. Sputtered films of very high resistance in the form of strips find use in electrical measurements. After aging they appear satisfactory if prepared properly.

Mercury arc still. Cowsik (55) suggests that Waran's (56) arc still for the purification of mercury is best adapted for the removal of metals such as magnesium or nickel which do not sputter readily.

Thin films and their properties. Many investigations have been made of the physical properties of thin films. In most of them the films were studied while resting on the glass plate support on which they were made. Their absorption for light, magnetic behavior, X-ray diffraction patterns, electrical and thermal resistance and surface appearance have been determined.

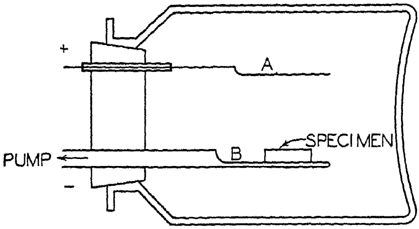

FIG. 82.—Apparatus for cathodic etching. Four-ounce bottle with cork. *A* = aluminum anode, *B* = copper tube serving as cathode, support of specimen and exhaust to vacuum pump. Smyth, Engineering **124**, 410 (1927).

An interesting observation by Ingersoll (57) indicates that such sputtered films may have quite remarkable chemical properties. A nickel film obtained by sputtering in nitrogen gave ammonia gas when heated afterwards in hydrogen above 150° C., showing that a nitride existed on the surface. As Ingersoll points out, many unusual compounds or quasi-compounds may be expected by similar actions between different metal-gas combinations.

Other forms of sputtering. Metals have been sputtered by heavy disruptive discharges, as for example in the explosion of fine wires by Anderson and Smith (58) and in certain experiments by Nagaoka and Futagami (59).

Gas disappearance in discharge tubes. Many investigators have studied the problem of gas disappearance in electrical discharge devices due to the passage of the electric current. The simplest view of the process seems to be that the phenomenon is due to the penetration of charged ions into the glass wall of the discharge vessel or the material of the cathode. The last-mentioned effect will cause the rupture of the cathode and the emission of larger crystals from the metal surface. This type of sputtering will no doubt take place under certain conditions, but the more usual phenomenon of sputtering is different in nature. If the cathode sputters it is also possible that the deposit formed will absorb considerable quantities of gas, leading to its temporary disappearance. Of course, if the nature of the cathode and the gas carrying the discharge is such that they can enter into chemical combination, gas disappearance due to the chemical reactions is possible. Since the rare gases can be cleaned up as well as the more chemically active ones, one would suppose that the actions involved are probably of a physical nature. The hardening of X-ray tubes is, of course, the same phenomenon.

In a series of investigations Campbell (60) working with the Research Staff of the General Electric Company of London studied the disappearance of gases in discharge tubes containing a hot-filament cathode. In nitrogen and carbon monoxide it is found to be proportional to the rate of ionization, independent of the pressure, the speed of the ionizing electrons and the arrangement of the electrodes. It depends greatly on the condition of the glass walls but not on their composition. The number of gas molecules disappearing is often greater than the number of ions present. Different gases behave somewhat differently. Even though it seems simplest to consider that ions are absorbed on the walls, becoming neutralized there, Campbell states that this view does not offer a complete picture of the situation. Perhaps neutral atoms or excited molecules produced in the discharge are the active species absorbed. The nature of the action between glass wall and absorbed gas is still obscure. A definite "glow potential" must be applied at a given pressure before "clean-up" becomes pronounced.

Since in our view the phenomenon is essentially a physical process of adsorption, unless the gases of the discharge obviously are of such a nature that chemical action may be expected, further attention to this interesting phenomenon would go beyond the scope of the present monograph. For this reason we have not mentioned the interesting controversy which existed at one time regarding the possible production of some of the rare gases from hydrogen in the electrical discharge. An excellent summary has been written by Pietsch (61).

From this review of the sputtering phenomenon we gain the idea that the disintegration of the cathode is in many cases responsible for chemical actions taking place in the discharge. While the phenomenon is considered at present to be a matter of local evaporation due to ion impact, it always is accompanied by gas disappearance. These two phenomena are very closely linked in character. It must be kept in mind that the chemical behavior of gases in the ionized and excited state is different from their behavior in the normal state. It is conceivable that chemical actions are involved where ordinarily one would not expect them.

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CHAPTER XX

MECHANISM OF CHEMICAL REACTIONS IN ELECTRICAL DISCHARGES

Ion clusters. As has been pointed out (page 173), any detailed theory of chemical reactions in electrical discharge will also have to fit the transformations produced by radon, because in both cases ionization occurs and is certainly the precursor of the chemical effects, whatever the detailed mechanism of the complete change observed may be. There is, however, one important difference between the two cases. The studies carried out in glow discharge and in electrodeless discharge are necessarily undertaken at low pressures (a few millimeters of mercury) while radon-induced reactions are carried out at higher pressures (about 1 atmosphere). Ozonizer studies are performed under similar pressure conditions, and one might expect that they should exhibit some analogy to the alpha-ray reactions. This particular point has been shown by Lind and Glockler (VII, 72) in the case of the condensation of hydrocarbons. Furthermore it should be pointed out that the oxidations of carbon monoxide and hydrogen under alpha-ray bombardment have been discussed satisfactorily by the cluster theory as ionic reactions and no other mechanism has so far been invented which would deal with these transformations in an acceptable manner. It is clear that in general the mechanism of reaction may be quite different when the pressure is changed a thousandfold, for at the higher concentrations triple collisions will be prominent and atomic species will be removed rapidly, giving them little or no opportunity to react. At any rate, the products may be quite different, depending on the pressure.

It will be of interest to note the various attempts that have been made to establish a reaction scheme for radon-activated systems and to consider its application to transformations occurring in electrical discharges. The two theories extant at the moment are the *ion-cluster theory*, which has been used on various occasions in discussing reactions, and the *atomic mechanism theory*. Both have yielded quantitative relations. Other suggestions involving metastable and excited structures and field catalysis will be mentioned although they have not been developed to any extent.

Dynamic clusters. The original cluster theory of Lind (I, 7) has been modified by several investigators. Mund (1–4) considered the interaction between the central ion and the clustered or coordinated molecules of the gas on the basis of the electrostatic forces acting between the charged ion and the permanent and/or induced dipoles of the neutral molecules. For an ion of charge e and molecules of total dipole moment μ this force, at distance R, is

$$F = \frac{2e\mu}{R^3} \tag{1}$$

Consider a molecule in the immediate neighborhood of the ion, attempting to leave it. Its kinetic energy is W. When

$$W < \int_{\rho}^{0} F dR \tag{2}$$

the molecule will be held by the attraction of the ion. Hence all molecules of energy W will be captured when they enter the region defined by the radius ρ:

$$\rho = \left(\frac{e\mu}{W}\right)^{1/2} = 9.1\ \text{Å} \tag{3}$$

if $W = 5.7 \times 10^{-14}$ erg = mean kinetic energy of a gas molecule at 0° C., $e = 4.774 \times 10^{-10}$ e.s.u. and $\mu = 1$ debye.

Since the average distance between molecules is 33 Å (N.T.P.), one notes that the radius of certain capture is about one-third of the distance between the molecules. Mund therefore takes the view that each ion is enveloped by a small region of gas density higher than the average concentration in the main body of the gas. In a mixture the proportions of molecules in the cluster will depend on their relative concentrations found there and on the permanent dipole moments of the constituents of the system and on their polarizabilities. The cluster pictured here is a dynamic agglomerate of molecules which will be constantly leaving the vicinity of the ion, being replaced by newcomers. While the molecules are in the neighborhood of the ion they are in a distorted or strained state and may be able to undergo reactions which they cannot enter into while in field-free space. In other words they are activated in the field of the ion. On neutralization the complex will fly apart, whatever configuration it happened to have, when the electron returned. This view differs from the earlier theories of Lind (I, 7), who considered that the activation energies derived from the heat of neutralization, i.e., chemical reaction, would ensue only on return of the electron. The molecules attached to the ion are still in motion; hence the designation "dynamic cluster." In their travel about the charged center, the molecules have opportunity of making impacts and rearranging themselves into new chemical configurations. The ion assumes the role of a catalyst. Günther and Cohn (5) favor this variant of the cluster theory. The molecules which are caught at large distances from the ion will not furnish a great deal of potential energy which might be used for activation within the cluster before the electron returns. If, however, they enter the first layer of molecules attached to the ion, considerable energy will be released, as can be seen from some calculations by Webb and Born on the hydration of ions cited by Van Arkel and de Boer (Chapter XV). In any case, the question arises regarding the process of formation of the cluster. There are attracting forces acting, but the energy must be removed if the cluster is to be stable. As usual it may leave the system as radiation, be taken away in a collision or be distributed into various degrees of freedom if the system is complex enough. In the dynamic cluster it is seen that the molecules already clustered will have to get their energy of activation from further attachments since the energy of recombination is not involved as in the static cluster.

The critical radius of the dynamic cluster. Rideal (6) and Mund (1) have attempted to calculate the radius of the dynamic cluster in terms of the dielectric constant of the gas. The induced dipole μ_i of a nonpolar molecule located in an electric field E is given by

$$\mu_i = \alpha E \tag{4}$$

where α is the polarizibility of the substance. Furthermore the Clausius-Mosotti relation for a gas which has a dielectric constant ε of about unity can be written

$$\varepsilon - 1 = (4\pi P \alpha)/kT \tag{5}$$

where P is the pressure and T is the absolute temperature. If the field near an ion ($E = e/r^2$) is used in these calculations,

$$\mu_i = \frac{(\varepsilon - 1)kT}{4\pi P} \cdot \frac{e}{r^2} \tag{6}$$

The force acting between the ion and the induced dipole is given by equation 3, whence the energy of interaction is

The critical radius is determined for the case that W is $\frac{3}{2}\,kT$:

$$\rho = \frac{(\varepsilon - 1)^{1/4}\, e^{1/2}}{(12\,\pi\,P)^{1/4}} \qquad (8)$$

If ε is always taken at 1 atmosphere

$$\rho = (\varepsilon - 1)^{1/4} \times 2.8 \times 10^{-7} \text{ cm.} \qquad (9)$$

This calculation is valid for non-polar molecules. Mund and Jungers (7) have used these considerations very successfully in discussion of radiochemical reactions.

Vapor pressure and stability of clusters. Besides the stoichiochemical cluster of Lind and the dynamic cluster of Mund more detailed considerations have been made concerning the constitution and stability of clusters. Quite a different point of view has been discussed by Livingston (8), who not only considers the cluster from the electrostatic basis but also develops the concept of the vapor pressure of a cluster. The ion cluster is treated as though it were a small drop in equilibrium with the surrounding gases. The fact that electric charges serve as centers of condensation, of water vapor for example, is well known from the behavior of a Wilson cloud chamber. When the electrostatic interaction is considered, the following relations are derived.

The density (Z) of a cluster, i.e., the number of molecules in the cluster per unit of its volume, is given by

$$Z = Z_0 \, exp\left(\frac{W}{kT}\right) \qquad (10)$$

where Z_0 is the concentration of molecules in the gas at a large distance from the ion. W is the work necessary to remove a molecule from the cluster, placing it in the main body of the gas, and is given by equation 7. From the gas laws

$$Z_0 = \frac{P}{kT} \qquad (11)$$

and if d_e = density of the clustered molecules in the first layer which will be of the order of magnitude of the density of the liquefied material

$$Z = \frac{d_e N}{M} \qquad (12)$$

where N = Avogadro's number and M = molecular weight. Combining these relations

$$P = \frac{d_e RT}{M} \, exp \left\{ (\varepsilon - 1)e^2 \right. \qquad (13)$$

gives the pressure of the gas in equilibrium with a one-layer cluster. N° is the number of molecules in unit volume at the pressure and temperature at which the dielectric constant is given.

If it is permissible to discuss the vapor pressure of such a small entity as an ion cluster, one can express the equilibrium between the clustered and the free molecules in the following manner (8). The cluster is a small drop, and its vapor pressure is

$$P_\rho = \quad exp \frac{2\gamma M}{RTrd_e} \qquad (14)$$

where P_∞ = vapor pressure of the clustered material as a liquid and γ = its surface tension. If both the effect of the charge-dipole interaction and the influence of the van der Waals forces are taken into consideration, then the vapor pressure P' is given by

$$P' = \quad exp \left\{ \frac{2\gamma M}{RTrd_e} - \frac{(\epsilon - 1)e^2}{8\pi N^\circ r^4 k} \right. \qquad (15)$$

This relation is illustrated in Table 32 for mole ions of bromine clustering hydrogen, bromine and hydrogen bromide. The remarkable situation indicated in this table is the great difference in pressure necessary to maintain a single-layer cluster of hydrogen bromide molecules on a bromine mole ion as compared with a double-layer: 6 × 10^{-6} and 10 atmospheres! The single-layer cluster is stable under ordinary pressure conditions, but the double-layer is to be expected only at much

TABLE 32

VAPOR PRESSURES OF BROMINE-CENTERED CLUSTERS

R. S. Livingston, Bull. soc. chim. Belg. **45**, 334 (1936)

Substance	Radius cm. × 10^8	Z/Z_0	P atm.	P_ρ atm.	P' atm.
H_2........	3.25	6.2	150.0		
HBr.......	3.55	8.5 × 10^6	8 × 10^{-5}	50.0	6 × 10^{-6}
Br_2........	4.00	1.2 × 10^3	0.4	4.1	3 × 10^{-3}
HBr*......	6.65	3.7	200.0	41.0	10.0

* Double layer.

higher pressures. Of course, the quantitative part of this theory is not to be taken too literally, but the fundamental concept is of the greatest interest to ion-induced reactions.

The ion-cluster equilibrium. In contrast to the ideas just presented indicating the stability of clusters, we find that Eyring, Hirschfelder and Taylor (9) believe that they are not a prominent feature of the mechanism of reaction. These investigators make a very interesting calculation of the equilibrium constant of cluster formation. The reaction

$$A + B^+ \leftrightarrows AB^+ \tag{16}$$

(A = neutral molecule, B^+ = ion, AB^+ = cluster) indicates the general type of interaction, and at equilibrium

$$\frac{[AB^+]}{[A]\cdot[B^+]} = K \tag{17}$$

is an expression of the mass-action law. This constant can be expressed in terms of the partition functions of the interacting species:

$$K = \qquad exp \tag{18}$$

$E_0 = -(\alpha e^2)/(2d^4)$ = the interaction energy between an ion of charge e and a polarizable molecule (polarizability α), distance d apart; $F_{\text{rot.}\,A}$, $F_{\text{rot.}\,B}$, $F_{\text{vib.}\,A}$, $F_{\text{vib.}\,B}$ = the rotational or vibrational parts of the partition functions of species A or B; $(8\pi^2\,kT\,I_{AB^+})/h^2$ = rotational partition function of species AB^+; I_{AB^+} = moment of inertia of AB^+;

$exp\ [(n +$ $\qquad\cdot / kT] = [2 \sinh (h\nu_{AB^+} / kT)]^{-1}$ = vibrational

0

partition function of species AB^+; $(2\pi\, m_{AB^+} kT)^{3/2} / h^3$ = translational part of partition function for species AB^+; m_{AB^+} = mass of cluster; M_A, M_B, M_{AB} = molecular weights; P_A = pressure in atmospheres of species A; a = polarizability in units 10^{-24} cc.; d = distance in Ångström units.

These expressions yield finally for the ratio of clustered to unclustered ion concentrations

$$\frac{[AB^+]}{[B^+]} = 6.46 \times 10^{-4} \left\{ \frac{M_A + M_B}{M_A \cdot M_B} \right. \tag{19}$$

The several clusters possible in the hydrogen system are given in Table 33. These calculations would indicate that the formation of clusters does not proceed to a great extent in the reactions involving hydrogen.

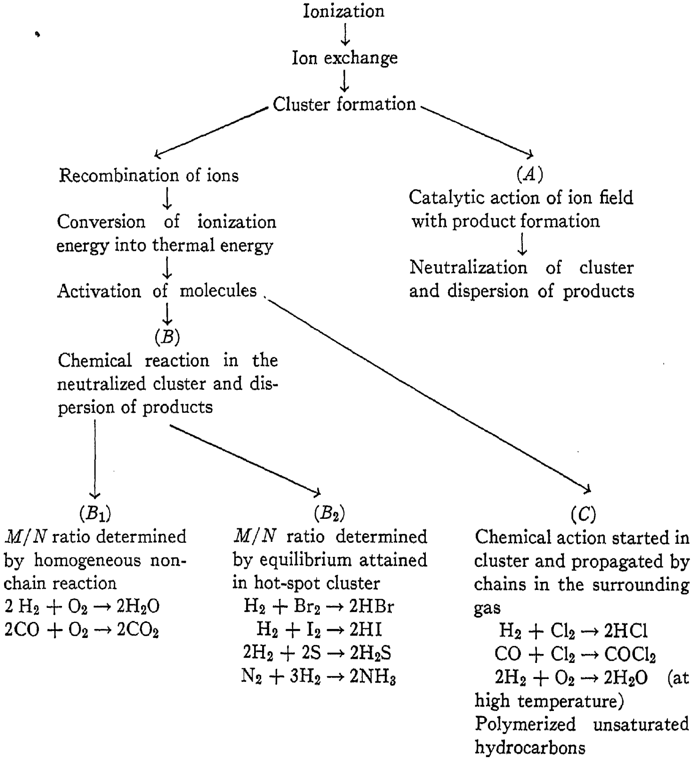
TABLE 33

CLUSTERS IN HYDROGEN

H. Eyring, J. Hirschfelder and H. S. Taylor, J. Chem. Phys. **4**, 479 (1936)
$d = 2.8\text{Å}$; $P_{H_2} = 1$ atm.

Cluster	a	Ratio of clusters to ions
$H_2 : H_2^+$	0.8	$[H_2 \cdot H_2^+]/[H_2^+] = 0.186$
$H : H_3^+$	0.663	$[H \cdot H_3^+]/[H_3^+] = 0.116$
$H_2 : H_3^+$	0.8	$[H_2 \cdot H_3^+]/[H_3^+] = 0.173$

General outline of cluster theory. The general concepts involved in the cluster theory of ion-induced reactions have been given by Livingston (8), based on the work of Lind (I, 7) and Mund (3). The reaction steps are:


Ionization
Ion exchange
Cluster formation
Recombination of ions
Conversion of ionization energy into thermal energy
Activation of molecules
(*B*)
Chemical reaction in the neutralized cluster and dispersion of products
(*A*)
Catalytic action of ion field with product formation
Neutralization of cluster and dispersion of products
(B_1)
M/N ratio determined by homogeneous non-chain reaction
$2H_2 + O_2 \rightarrow 2H_2O$
$2CO + O_2 \rightarrow 2CO_2$
(B_2)
M/N ratio determined by equilibrium attained in hot-spot cluster
$H_2 + Br_2 \rightarrow 2HBr$
$H_2 + I_2 \rightarrow 2HI$
$2H_2 + 2S \rightarrow 2H_2S$
$N_2 + 3H_2 \rightarrow 2NH_3$
(C)
Chemical action started in cluster and propagated by chains in the surrounding gas
$H_2 + Cl_2 \rightarrow 2HCl$
$CO + Cl_2 \rightarrow COCl_2$
$2H_2 + O_2 \rightarrow 2H_2O$ (at high temperature)
Polymerized unsaturated hydrocarbons

The possible mechanism (*A*) has already been considered. The other classification leads to two main groups: (*B*) reactions which occur in the cluster and (*C*) reactions which start in the cluster and spread by some chain mechanism through the body of the gas. Class (*B*) can be separated into two main groups: (B_1) involves large changes in free energy, and such reactions should be practically irreversible. They should be independent of temperature. Group (B_2) on the other hand includes reactions of small free energy change, and such reactions may attain equilibrium in the cluster.

The hot-spot theory of ion reactions. Reactions due to excited molecules and atoms produced by dissociation are of minimal importance in ionic reactions, in the opinion of Livingston, who developed the "hot-spot" theory of cluster reaction (8). This type of mechanism was tested by Lind and Livingston (10) in respect to hydrogen bromide synthesis and decomposition. They studied these reactions with varying relative amounts of hydrogen, bromine and hydrogen bromide.

The theory is called the "hot-spot" theory because the central idea involves the concept of a high-temperature region about the cluster where reaction takes place. The detailed mechanism is as follows: An ion (either positive or negative), produced by any means whatever, will cluster other molecules in accordance with their dipole nature, their polarizabilities and their relative amounts. No reaction occurs until neutralization sets in, when the large recombination energy becomes available, which raises the cluster to a "high temperature." Perhaps it is better to say that the cluster now has an energy content which it could attain only if it existed at some equivalent high temperature as a large body of gas. Of course it is realized that the few molecules concentrated in the cluster are insufficient to define temperature in the usual statistical manner. Furthermore it is evident that applications of equilibrium considerations are to be thought of as equivalent situations in the sense that many clusters together would have a sufficient number of molecules so that statistically they could attain equilibrium in the thermodynamic sense. On this basis it is supposed that the energy of recombination spreads over the whole cluster, activating bonds and hence initiating chemical reactions. In this energy-rich or hot cluster, equilibrium will be established and the whole agglomerate will separate into the reaction products. This picture describes only the average behavior of a cluster, since, for example, it is quite possible that some clusters decompose into the original reactants and the ionization energy appears as heat. In this case a certain inefficiency would result. However, only the average behavior leading to chemical reaction is of interest, and the following relations will give this theory in the case of hydrogen bromide synthesis:

$x(H_2)$, $x(Br_2)$, $x(HBr)$ = mole fractions in the cluster immediately before recombination.

$P(H_2)$, $P(Br_2)$, $P(HBr)$ = pressures of the reactants.

α, β = constants which specify the enrichment of bromine and hydrogen bromide relative to hydrogen in the cluster.

M/N = the change in hydrogen bromide molecules in an average cluster due to attainment of equilibrium after recombination.

n = total number of molecules of all kinds in the average cluster.

x' = mole fractions after attainment of equilibrium (at some equivalent high temperature).

K = equilibrium constant (at some equivalent high temperature).

Then

$$x(H_2) = \frac{P(H_2)}{P(H_2) + \alpha P(Br_2) + \beta P(HBr)}, \text{ etc.}$$

and

$$x'(H_2) = x(H_2) - \frac{M}{2nN}, \text{ etc.}$$

Writing the mass-law expression leads to an equation for M/N in terms of the pressures of the reactants and four adjustable constants. $\alpha = 38$, $\beta = 15$, $K = 2.2$ and $n = 8$ were used to fit the experimental data. The values chosen are reasonable when their meaning is considered. The results are shown in Table 34. Livingston was also able to fit the hot-spot theory to the condensation of acetylene and to the rare-gas-ion sensitized reactions. So far no other theory has dealt with ionic reactions with greater success, and the same ideas will have to be applied to gas-discharge reactions.

On the other hand it is extremely interesting to note that the case just cited has been treated by an entirely different theory involving an atomic mechanism, and at present it appears that this mode of reaction is perhaps plausible. It may well turn out, as in so many cases, that a proper combination of certain features of the two rival theories will lead to an ultimately acceptable explanation.

Atomic mechanism. The reactions in discharge or by alpha radiation may be considered on the basis of a non-cluster mechanism in opposition to the views just outlined. We have seen that atoms and radicals are produced in electrical discharge in abundance and they most probably occur also in a gas under the influence of radon. The reactions of atomic hydrogen, oxygen, nitrogen and chlorine studied in flow systems and in the post-discharge have their ready explanation on the basis of an atom mechanism (Chapter VI). Hence it is proper to review the attempts made to explain all ion-induced reactions by processes involving atoms and no ion clusters. Two cases have been discussed by Eyring, Hirschfelder and Taylor (9): the ortho-para-hydrogen conversion, and the synthesis and decomposition of hydrogen bromide.

In the field of discharge reactions Emeléus and Lunt (11, 12) have approached the problem by considering the statistical theory of such reactions. They have rendered a definite service by carefully discussing many important quantities which should be useful in determining chemical changes in discharge. Their study inclines them to the belief that " the first step of such reactions takes place between a reactant molecule unaffected by the discharge and a neutral product of an electron collision with such a molecule." In other words, Emeléus and Lunt consider the reaction partners to be neutral molecules and the reaction to be related to the conductivity of the gas only incidentally in the same way as is a great part of the luminosity of the discharge. The charged particles have no direct connection with the chemical transformation taking place.

This kind of theory is incapable of explaining quantitatively the effect of foreign gases in such reactions as the polymerization of acetylene, cyanogen and hydrogen cyanide by alpha particles. On the other hand it is of interest to recall at this point that Finch (13) claims that neutral sputtered metal atoms from the cathode initiate the cathodic combustion of hydrogen and carbon monoxide.

Para to ortho hydrogen conversion. The ion species produced in hydrogen gas are known from mass-spectrographic studies (Chapter XVII). The mole ion (H_2^+) is formed most readily by direct interaction of electrons and hydrogen molecules. The triatomic mole ion (H_3^+) owes its existence to a further collision:

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

It should be especially prominent at the high pressures employed in radiochemical and ozonizer reactions. Eyring and co-workers (9) estimate the absolute rate of formation of H_3^+ and they find it

1.25×10^{15} cc. per mole per sec.—a very high value, so that the triatomic ion must be considered in the reaction mechanism.

On the basis of their calculations on cluster formation (page 435) they decide that any mechanism involving clusters is not of importance in the conversion of para to ortho hydrogen. It is seen that such calculations lead to the view that only 1 ion in 5 to 9 is clustered.

The formation of negative ions (H_2^-) is also considered by them, but it is not expected that such ions will occur in abundance because the stable state of H_2^- cannot be reached by electron collision in hydrogen. On the other hand, neutralization processes:

will yield hydrogen atoms. If their relative probability is taken into account it appears that at least 3 to 4 hydrogen atoms are produced per ion pair. Furthermore, excitation processes in the track of the alpha particle may augment this ratio to 6 hydrogen atoms per ion pair. Direct conversion by the alpha particle of para- to ortho-hydrogen on account of the magnetic field due to the motion of the alpha particle is neligible, as is also the direct conversion due to the paramagnetism of H_3^+, H_2^+ and H atoms according to Wigner (14). The only mechanism which remains for the conversion of para- to ortho-hydrogen is a direct exchange reaction between atomic hydrogen and the para-hydrogen molecule:

$$H + H_2(p) \rightarrow H_2(o) + H$$

Having excluded all other processes, Eyring and co-workers believe that hydrogen atoms formed by alpha particles carry on the conversion by the chain reaction indicated.

Synthesis and decomposition of HBr. Just as in the conversion of para-hydrogen, Eyring and co-workers (9) consider that the ionic reactions induced by the passage of an alpha particle liberate hydrogen atoms, and again they estimate that about 6 such atoms are produced per ion pair. In the mixture of gases involved in the present synthesis, all sorts of ions and atoms are possible and have actually been found in mass-spectrographic studies or have been surmised in chemical reactions: for example, bromine atoms. But none are important in the present reaction mechanism except hydrogen atoms, which may react with either hydrogen bromide or bromine:

$$H + Br_2 \quad (k_3) \quad HBr + Br + 36\ \text{k-cal.}$$

$$H + HBr \qquad\qquad H_2 + Br + 16\ \text{k-cal.}$$

The relative rate (k_3/k_4) of these two reactions is known to be 8.4 from the work of Bodenstein and Jung (15).

The chance (B) that a hydrogen atom will react with bromine to form hydrogen bromide rather than destroy one molecule of hydrogen bromide is

$$B = \frac{k_3\,(\mathrm{Br_2})}{k_4(\mathrm{HBr}) + k_3(\mathrm{Br_2})}$$

$$= \frac{1}{1 + (1/8.4)\,(P_{\mathrm{HBr}}/P_{\mathrm{Br_2}})}$$

The reactions of bromine atoms with hydrogen and hydrogen bromide molecules are endothermic and need not be considered. Electrons may be captured by bromine or hydrogen bromide molecules:

$$\mathrm{E^-} + \mathrm{Br_2} \rightarrow (k_1) \rightarrow \mathrm{Br^-} + \mathrm{Br};\ \mathrm{E^-} + \mathrm{HBr} \rightarrow (k_2) \rightarrow \mathrm{Br^+} + \mathrm{H}$$

The relative importance of these two reactions can be expressed by the probability

$$A = \frac{k_2(\mathrm{HBr})}{k_1(\mathrm{Br_2}) + k_2(\mathrm{HBr})} \qquad \frac{1}{(k_1/k_2)}$$

Consider that in a mixture of hydrogen, bromine and hydrogen bromide a hydrogen atoms are produced from the alpha particles through some process of ionization and/or dissociation. When the initial energy of the alpha particle is taken up by b hydrogen bromide molecules, then b atoms of hydrogen are produced. The total number of hydrogen atoms formed is

$$aN_{\mathrm{H_2}} + bN_{\mathrm{HBr}} + AN$$

and the number of hydrogen bromide molecules decomposed directly is

The yield of hydrogen bromide per ion pair is

$$\frac{M}{N} \qquad\qquad \frac{}{N} \qquad\qquad \frac{N_{\mathrm{HBr}}}{N} - 2A(1 - B)$$

Eyring and co-workers were able to account for the observed M/N ratios by choosing $a = 6$, $b = 2$ and $A = 1$ for large ratios of $P(\mathrm{HBr})/P(\mathrm{Br_2})$. We have then the interesting situation that the same set of experimental data (Table 34) can be accounted for by two

TABLE 34

HYDROGEN BROMIDE SYNTHESIS AND DECOMPOSITION
(Molecules HBr appearing per ion pair)

Experiment	Experimental value	Ion-cluster theory, Lind and Livingston (8, 10)	Atomic mechanism, Eyring, Hirschfelder and Taylor (9)
1	0.24	0.27	0.24
2	0.42	0.42	0.39
3	0.58	0.51	0.48
4	0.88	0.86	0.84
5	1.90	1.81	1.79
6	1.76	2.02	1 98
7	2.67	2.16	2.27
8	2.76	2.64	2.83
9	2.85	2.77	2.98
10	2.85	2.70	2.99
11	2.89	2.91	3.47
12	−0.89	−0.19	−0.17
13	−3.98	−4.03	−4.70
14	−3.57	−3.42	−3.44
15	−2.57	−2.00	−3.85
16	−5.07	−2.18	−5.74

quite different mechanisms. The difficulty, of course, lies in the great complexity of reaction possibilities when activation occurs by either radon or in electric discharge.

Excited, metastable molecules and atoms. The formation of nitric oxide from the elements is considered by Willey (16) to involve metastable molecules of oxygen in the $^1\Sigma_g^+$ state. He finds some objections to all mechanisms contemplated so far for the reaction of oxygen and nitrogen in electrical discharges, and, by elimination of ion-cluster and atomic processes, he attempts to establish as the important step in the reaction

$$N_2 + O_2\ (^1\Sigma_g^+) \rightarrow 2NO$$

The detailed picture as to the production of these metastable molecules has not been worked out, but they are most probably the result of collisions. The suggested mechanism is interesting and it should be compared with the controlled electron reactions of oxygen (Chapter V). The ions are regarded as the forerunners of the chemically reactive species (17).

In radon-activated reactions, Mund (3) pointed out that the ionic reaction may be accompanied by photochemical transformations and that even rare-gas catalysis can be understood on a non-ion basis if it is supposed that activation energies can be transmitted from molecule to molecule. But it is of interest to note that Rollefson and Potts (18) state that normal chlorine atoms are more reactive towards iodine monochloride than are excited chlorine atoms in the $^2P_{1/2}$ state. It is not a foregone conclusion, then, that excited states are more active than the ground state. Resonated oxygen atoms (^1D) do not seem to be much more reactive toward hydrogen or methane than normal ones, as was mentioned by Kistiakowsky and Millington (19). The theory of discharge reactions has also been discussed by Vasilev, Kobozev and Eremin (20) and by Nekrasov (21).

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